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THERMODYNAMIC STUDIES OF THE EFFECTS OF SOLVENTS ON MOLECULAR COMPLEX FORMATION EQUILIBRIA; ORIENTATION OF WATER AROUND NONPOLAR SOLUTES IN AQUEOUS SOLUTIONS.

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THERMODYNAMIC STUDIES OF THE EFFECTS OF SOLVENTS ON MOLECULAR COMPLEX FORMATION EQUILIBRIA; ORIENTATION OF WATER AROUND NONPOLAR SOLUTES IN AQUEOUS SOLUTIONS.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

CHAPTER I

INTRODUCTION

As early as the late nineteenth century, the rates and equilibria of certain reactions were found to be changed as the media were changed. The failure of the assumption that solvents are inert in the reaction systems led to various attempts to explain the observed solvent effects. Bulk properties of solvents, such as the viscosity and the dielectric constant, were considered in relation to the influence of solvents on the reaction systems. Soper and Williams[1] suggested that polar solvents accelerate reactions producing polar products and have the opposite effect when the resultants are less polar than the reactants. In fact, early experiments[2,3] showed that solvents of high dielectric constant favor reactions in some cases and retard reactions in other cases. Davies and coworkers[4,5] attempted to show that the free energy and the enthalpy of dimerization of fatty acids vary linearly with the inverse of the dielectric constant of the solvent. Franzen and coworkers[6,7] also found the linear relationship to be obeyed in the interamide hydrogen-bonded complex formation between N-methylacetamide and ε-caprolactam and Hirano and Kozima[8] reported such a relation in the case of the molecular complex formation reaction between triethylamine and methyl alcohol. Norrish and Smith[9] proposed that solvent

molecules rob the reactants of their critical energy in deactivating collisions in the formation of a molecular complex between trimethylamine and m-and p-nitrobenzyl choloride in benzene solution, respectively.

$$\text{m- or p-}NO_2C_6H_4CH_2Cl + (CH_3)_3N \rightarrow \text{m- or p-}NO_2C_6H_4CH_2Cl\cdot N(CH_3)_3$$

In the experiments of Cox[10] and Hawkins[11] on the molecular complex formation reactions of the stystems

$$C_6H_5NH_2 + p\text{-}BrC_6H_4COCH_3 \rightarrow C_6H_5NHC_6H_4COCH_3HBr$$

$$C_5H_5N + C_3H_5Br \rightarrow C_5H_5N\cdot C_3H_5Br$$

the fact that the observed rate constants in the vapor phase, in the solvent carbon tetrachloride, and in the solvent hexane are of the same order of magnitude showed that the effect is not due to deactivation by solvent molecules.[12] However, the ratio of the observed rate constants to the calculated rate constants of hypothetical gas reactions having a given activation energy was found to be greater with polar solvents than with nonpolar solvents. The viscosity of the solvents[13-15] was thought to play an important role in molecular complex formation reactions. Although the frequency of collision between reactant molecules will not be influenced much by the viscosity of the media, collisions between solute and solvent molecules may be increased by an increase in the viscosity of the solvents.

Buchowski, et al.,[16] and Huong, et al.,[17] showed experimentally the relationship

$$\log_{10} K_c = a + b\,\delta_s \qquad (1)$$

is approximately followed in the complex formation reactions

$$C_5H_{11}-C\equiv C-H + O=C(CH_3)_2 \rightleftarrows C_5H_{11}-C\equiv C-H \cdot O=C(CH_3)_2$$

$$I_2 + C_5H_5N \rightleftarrows I_2 \cdot C_5H_5N$$

where K_c is the equilibrium constant in ℓ/mole, δ_s the solubility parameter in cal $^{1/2}$ cm$^{-3/2}$, and a and b are constants dependent only on the properties of the electron donor and acceptor. Similar relations involving solubility parameters have been discussed previously by Hildebrand and Scott,[18] Scatchard,[19] Flory,[20,21] and Huggins.[22]

The ionization potentials of solvents appear to influence values of equilibrium constants of charge-transfer complex formation reactions. Equilibrium constants of complexes between naphthalene and s-trimethylbenzene[23] and between 1,3,5-trinitrobenzene and hexamethylbenzene, pentamethylbenzene, durene, mesitylene, or benzene[24] decrease in the order of solvents c-hexane > n-hexane > carbon tetrachloride > CS_2 > chloroform which is the order of decreasing ionization potentials of solvents. Decrease of the equilibrium constant in the solvent chloroform has been attributed to competitive complex formation between the electron donor and solvent; a weaker solvent-donor interaction is thought to occur in CCl_4.[24]

The possibility of weak complex formation between the solvent and the reacting species was proposed to explain solvent effects, and the interaction between solute and solvent molecules has been studied. In earlier studies, solvents like hydrocarbons and ethers were called the "slow" solvents and solvents like alcohols and ketones the "fast" solvents according to the solvent influence on specific chemical

effects, such as in the formation of tetraethyl ammonium iodide molecules.[25]

$$(C_2H_5)_3 N + C_2H_5 I \rightleftharpoons (C_2H_5)_4 N I$$

It was concluded that the interaction between solute and solvent molecules is least in the aliphatic hydrocarbon solvents and greatest in the aromatic alcohols. In dealing with chemically active solvents, the following two models have been tried in treating equilibrium data for electron donor-acceptor molecular complex formation.

The equilibrium between the electron donor and acceptor molecules and the product charge-transfer complexes was studied with a model[26] in which components are solvated and the solvated components are in equilibrium in the following manner:

$$AS_a + D \rightleftharpoons ADS_b + qS \qquad (2)$$

where A, D, and AD are the electron acceptor, the electron donor, and the adduct, respectively, S denotes the solvent, a and b are the number of solvent molecules attached to components, and q is the number of free solvent molecules involved in the equilibria. Here, for simplicity, D is not considered to be specifically solvated. Another model[27,28] is that A, D, and AD are each assumed to be in equilibrium with solvated species and that the equilibrium reaction can be written as

$$AS_a + DS_m \rightleftharpoons ADS_b + Sq \qquad (3)$$

where the relationship among a, m, b and q must be $q = a + m - b$.

Benson[29] explains the change of kinetic rate constants for solution reactions by employing the transition state theory in combination with the free volume model of a liquid.

The aims of the present research are to develop a suitable model for predicting the effects of solvents on the equilibrium constants of charge-transfer or hydrogen-bonded molecular complex formation reactions in nonpolar solvents and to elucidate the singular behavior of nonpolar solutes in aqueous solutions by relating these anomalies to the abnormally oriented layer of water molecules around the solute molecule.

CHAPTER II

ENERGIES AND FREE ENERGIES OF SOLVATION AND THEIR EFFECTS ON MOLECULAR COMPLEX FORMATION EQUILIBRIUM CONSTANTS

The following solvation cycle[36] is useful in studying the influence of solvents on equilibrium constants of the molecular complex formation between an electron donor (D) and an electron Acceptor (A) molecule:

$$\begin{array}{ccccc} D(v) & + & A(v) & \underset{\Delta E^{o}(v)}{\overset{\Delta G^{o}(v)}{\rightleftharpoons}} & DA(v) \\ \Delta E^{o}_{v\to s,D}\downarrow \uparrow \Delta G^{o}_{s\to v,D} & & \Delta E^{o}_{v\to s,A}\downarrow \uparrow \Delta G^{o}_{s\to v,A} & & \Delta E^{o}_{v\to s,DA}\downarrow \uparrow \Delta G^{o}_{s\to v,DA} \\ D(s) & + & A(s) & \underset{\Delta E^{o}(s)}{\overset{\Delta G^{o}(s)}{\rightleftharpoons}} & DA(s) \end{array}$$

where v and s in parenthesis denote the vapor phase and the solvent phase, respectively. The cycle relates energies and free energies of solvation to energies and free energies of the complex formation reaction. For example, the relations between the solution phase and gas phase thermodynamic quantities for the complex reaction are:

$$\Delta G^{o}(s) = \Delta G^{o}(v) + \Delta G^{o}_{v\to s,DA} - \Delta G^{o}_{v\to s,D} - \Delta G^{o}_{v\to s,A} \qquad (4)$$

$$\Delta E^{o}(s) = \Delta E^{o}(v) + \Delta E^{o}_{v\to s,DA} - \Delta E^{o}_{v\to s,D} - \Delta E^{o}_{v\to s,A} \qquad (5)$$

where $\Delta G^{o}(s)$ and $\Delta G^{o}(v)$ are standard free energy changes of the reaction

in the solution phase and in the gaseous phase, respectively. The standard states adopted here are those of the unit molarity of ideal gas for gaseous species and the unit molarity of ideal dilute solute states in the solvent phase. Therefore $\underset{v\to s,i}{\Delta G^{o}}$ represents the free energy change of the process in which one mole of the species i is transferred from the state of 1 molar ideal gas to the state of one molar ideal infinitely dilute solution in the solvent. Likewise, $\Delta E^{o}(s)$ and $\Delta E^{o}(v)$ are the standard internal energy changes for the solution phase reaction and for the gaseous phase reaction, respectively and $\underset{v\to s,i}{\Delta E^{o}}$ represents the internal energy change when one mole of the species i is transferred from the ideal gas to the ideal infinitely dilute solution in the solvent. The five equilibrium constants involved in the solvation cycle are written

$$K_c^{(v)} = [DA(v)] \,/\, [D(v)]\,[A(v)] \tag{6}$$

$$K_c^{(s)} = [DA(s)] \,/\, [D(s)]\,[A(s)] \tag{7}$$

$$K_{D,D} = [D(s)] \,/\, [D(v)] \tag{8}$$

$$K_{D,A} = [A(s)] \,/\, [A(v)] \tag{9}$$

$$K_{D,DA} = [DA(s)] \,/\, [DA(v)] \tag{10}$$

where $K_c^{(v)}$ and $K_c^{(s)}$ are the complex formation equilibrium constant in the gaseous phase and in the solution phase, respectively, K_D denotes the distribution constant of the respective species between the gaseous phase and in the solvent, and the bracket denotes the molar concentration of the individual species. (The systematic change of $K_{D,i}$ values for various solutes in a given solvent is discussed in the Appendix I.)

The substitution of the relationships

$$\Delta G^{o}(v) = -RT\ell nK_{c}^{(v)} \tag{11}$$

$$\Delta G^{o}(s) = -RT\ell nK_{c}^{(v)} \tag{12}$$

$$\Delta G^{o}_{v\rightarrow s,D} = -RT\ell nK_{D,D} \tag{13}$$

$$\Delta G^{o}_{v\rightarrow s,A} = -RT\ell nK_{D,A} \tag{14}$$

and

$$\Delta G^{o}_{v\rightarrow s,DA} = -RT\ell nK_{D,DA} \tag{15}$$

into equation 4 leads to

$$K_{c}^{(s)} = K_{c}^{(v)} \left[K_{D,DA}/(K_{D,D}\, K_{D,A})\right] \tag{16}$$

The factor $K_{D,DA}/(K_{D,D}\, K_{D,A})$ varies from solvent to solvent and it will determine changes in the equilibrium constants in the solvent phase as compared to the gaseous phase. To predict the value $K_{D,DA}/(K_{D,D}\, K_{D,A})$ Christian, et al.,[30,32,36] devised parameters designated as α and α' which were defined as

$$\alpha = \frac{\Delta E^{o}_{v\rightarrow s,DA}}{\Delta E^{o}_{v\rightarrow s,A} + \Delta E^{o}_{v\rightarrow s,D}} \tag{17}$$

$$\alpha' = \frac{\Delta G^{o}_{v\rightarrow s,DA}}{\Delta G^{o}_{v\rightarrow s,A} + \Delta G^{o}_{v\rightarrow s,D}} \tag{18}$$

respectively, and they attempted to avoid the necessity of obtaining experimental information about $\Delta E^{o}_{v\rightarrow s,DA}$ and $\Delta G^{o}_{v\rightarrow s,DA}$ since these values are not so easily obtainable as those of $\Delta E^{o}_{v\rightarrow s,A}$, $\Delta E^{o}_{v\rightarrow s,D}$, $\Delta G^{o}_{v\rightarrow s,A}$, and $\Delta G^{o}_{v\rightarrow s,D}$.

In weak molecular complexes[30,32] α and α' were predicted to be nearly equal, but less than unity,[36] and this has generally been

observed empirically,[31-33] although strong charge-transfer complexes like trimethylamine·SO_2 and triphenylarsine·I_2 give α and α' values larger than unity.[30,32,39] The occurrence of α and α' values larger than unity is attributed to the extra dipole moment produced in the complex compared to the vectorial sum of the dipole moments of the component molecules; the large dipole moment of the complex more than compensates for the effect of the squeezing out solvent as the complex forms from the solvated monomers.[30,32] α and α' values remain nearly the same for a given complex formation reaction in a series of different solvents. A test of the constancy of α and α' can be devised by the following analysis. Combination of equation 4 and relationships

$$\Delta G^{o}_{v\rightarrow s,DA} = \alpha' \left(\Delta G^{o}_{v\rightarrow s,A} + \Delta G^{o}_{v\rightarrow s,D}\right) \tag{19}$$

and

$$\Delta G^{o} = -RT\ln K_c \tag{20}$$

where K_c is an equilibrium constant results in the relation

$$K_c^{(s)} = K_c^{(v)} \left(K_{D,D}\, K_{D,A}\right)^{\alpha'-1} \tag{21}$$

Equation 21 predicts that plotting of $\log_{10} K_c^{(s)}$ vs $\log_{10} (K_{D,D}\, K_{D,A})$ for various solvents will give a straight line with a slope of $\alpha'-1$ and an intercept of $\log_{10} K_c^{(v)}$. In Figures 1, 2, and 3 the near-constancy of α' is shown by the linearity of plots of $\log_{10} K_c^{(s)}$ with $\log_{10} (K_{D,D}\, K_{D,A})$. Therefore, knowledge of α', $K_{D,D}$, and $K_{D,A}$ will enable prediction of $K_c^{(s)}$ values from $K_c^{(v)}$ values, thus making it possible to avoid the rather difficult procedures for obtaining the $\Delta E^{o}_{v\rightarrow s,DA}$ and $\Delta G^{o}_{v\rightarrow s,DA}$ values from equilibrium data.

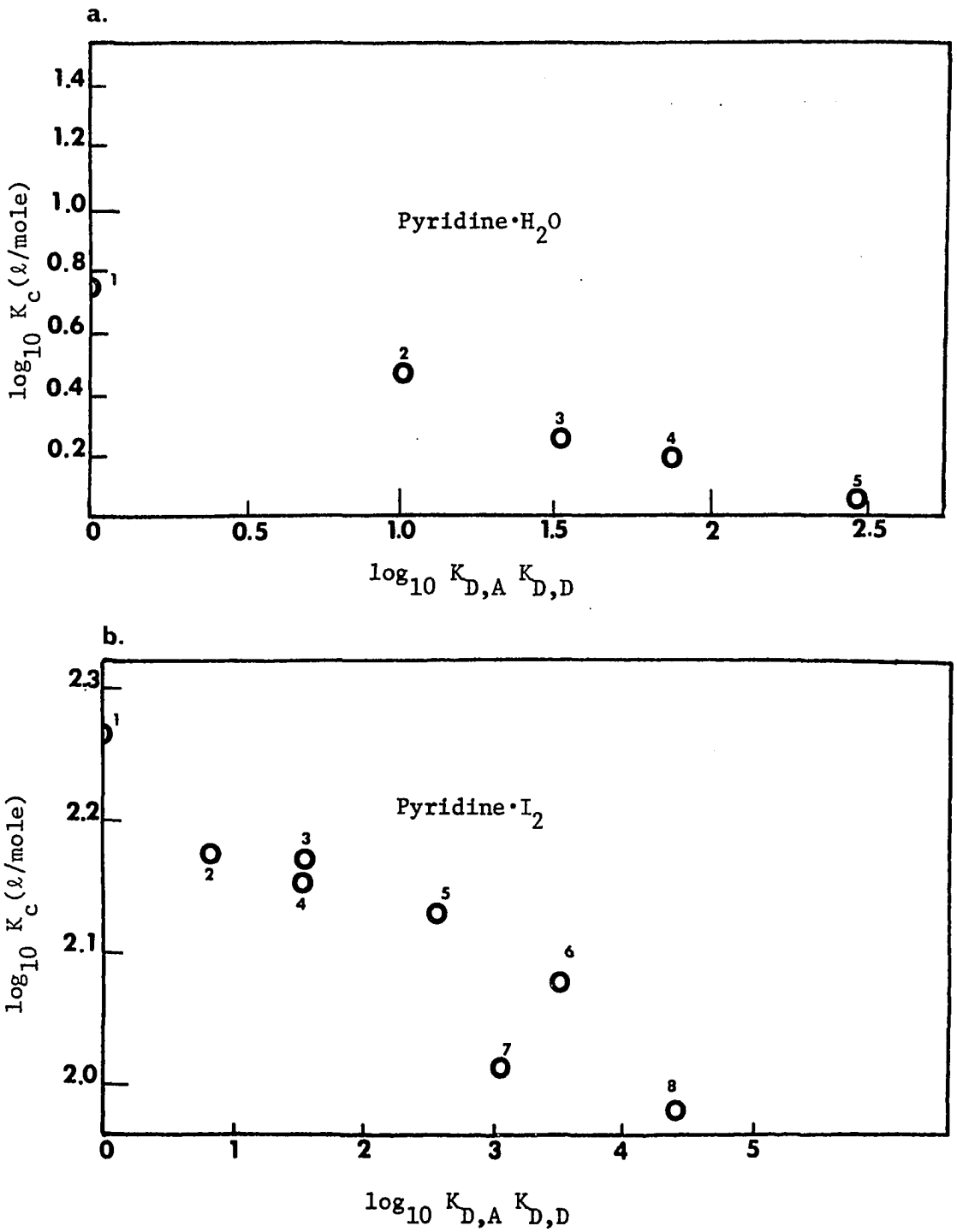


Figure 1: Correlation of formation constant with distribution constants of donor and acceptor for reactions pyridine + water = pyridine·water and pyridine + iodine = pyridine·iodine at 25°C. [149]

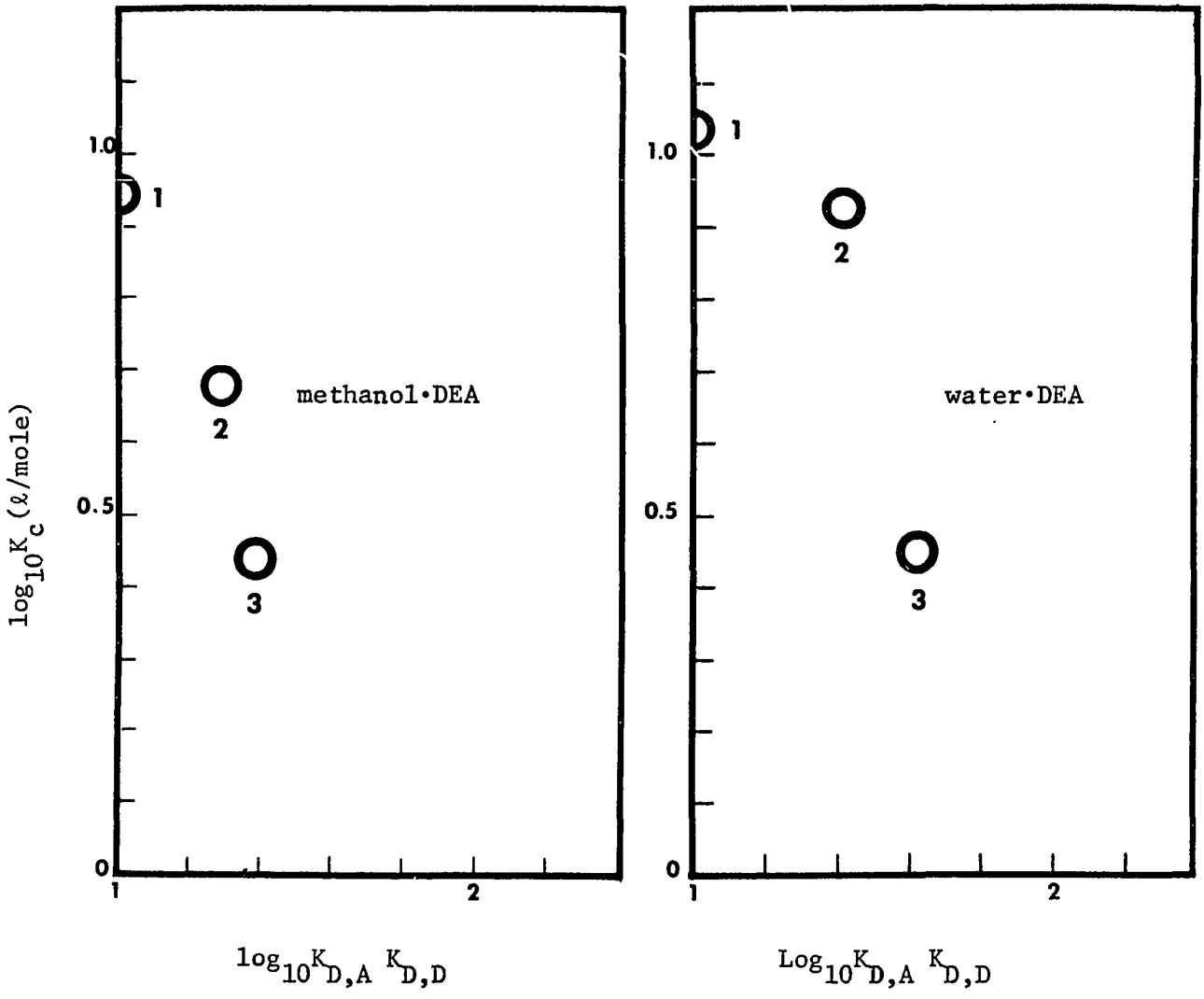


Figure 2: Correlation of formation constant with distribution constants of donor and acceptor for reactions methanol + diethylamine = methanol•diethylamine and water + diethylamine = water• diethylamine at 25°C.[150]

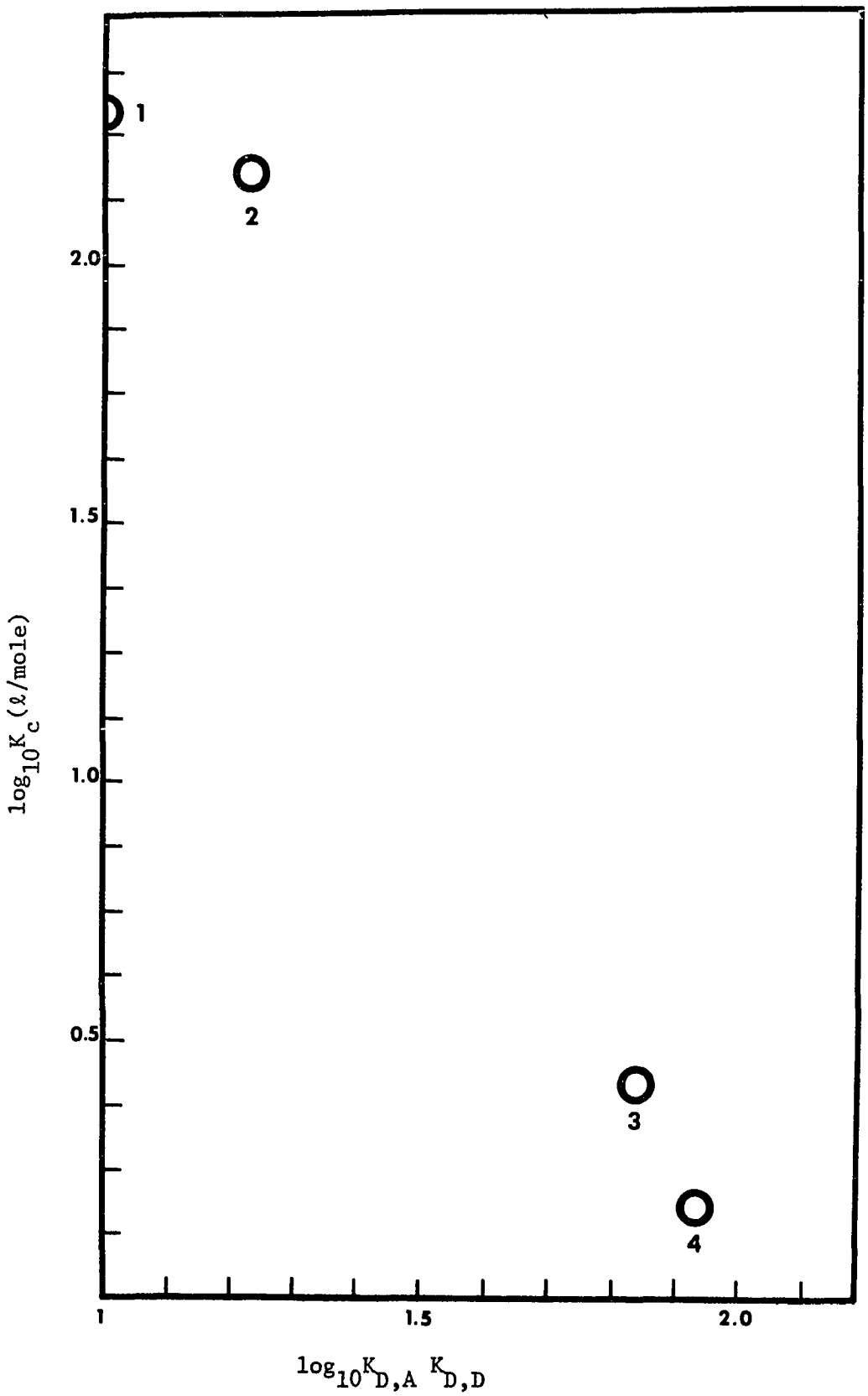


Figure 3: Correlation of formation constant with distribution constants of donor and acceptor for the reaction 2 TFA = $(TFA)_2$ at 25°C.[151]

LEGEND FOR FIGURES 1-3

Figure 1a. 1, cyclohexane (reference solvent); 2, carbon tetrachloride; 3, toluene; 4, benzene; 5, 1,2-dichlorethane.

Figure 1b. 1, squalane (reference solvent); 2, i-octane; 3, hexane; 4, heptane; 5, cyclohexane; 6, tetrachloroethylene; 7, carbon tetrachloride; 8, carbon disulfide.

Figure 2. 1, hexadecane (reference solvent); 2, diphenylmethane; 3, benzylether.

Figure 3. 1, cyclohexane (reference solvent); 2, carbon tetrachloride; 3, benzene; 4, dichloroethane.

The values of $\log_{10} K_{D,A}\ K_{D,D}$ are normalized to unity for reference solvents in Figures 2 and 3: in Figure 1 the values of $K_{D,A}\ K_{D,D}$ are normalized to unity for reference solvents.

α' may be obtained from either experimental values or calculated values. First, if α' is assumed to be constant, its value can be determined from two sets of experimental values of $K_c^{(s)}$, $K_{D,D}$, and $K_{D,A}$ for two different solvents, respectively. Secondly, with the assumption of the equality of α' and α, which is ordinarily reasonably good, $\underset{v\to s,i}{\Delta E^o}$ (and hence α) can be calculated by the method of Stevens, et al.,[31,32,40] which uses a simple quasi-lattice model of solution incorporating interaction energy parameters for each designated solute-solvent contact site. The calculated parameters may be used to obtain $\underset{v\to s,i}{\Delta E^o}$ values for a wide variety of systems having the same types of contact sites. However, this method is not good for systems in which solvents are active or the complexes formed attain significant additional dipole moment during the formation process. Experimental values of α and α' are given in Table 1.

Since the nineteen thirties, various empirical linear relationships between the entropy of vaporization and the enthalpy of vaporization has been proposed and discussed in terms of various types of solutes behavior.[37,67] Christian and Grundnes[32,34] observed that a convenient linear relation exists between $\underset{v\to s,i}{\Delta G^o}$ and $\underset{v\to s,i}{\Delta E^o}$ for various solutes in most unassociated solvents:

$$\underset{v\to s,i}{\Delta G^o} = \beta_s \underset{v\to s,i}{\Delta E^o} + 300 \quad \text{cal/mole} \tag{22}$$

where β_s values vary slightly from solvent to solvent, but center around 0.6. Interestingly enough, the intersection point is in all cases very nearly 300 cal. Examples of the linearity are shown in Figues 4, 5, and 6 (Note that equation 22 is not valid for water as the solvent). There-

TABLE 1

EXPERIMENTAL VALUES OF α AND α' FOR TYPICAL MOLECULAR COMPLEXES AT 25°C[129]

Complex	Solvent	α	α'
$(CF_3COOH)_2$	cyclohexane	0.72	0.55
$(CF_3COOH)_2$	CCl_4	0.59	0.55
$(CF_3COOH)_2$	benzene	0.43	0.39
$(CF_3COOH)_2$	1,2-dichloroethane	0.48	0.39
pyridine·H_2O	a	-	0.71
diethylamine·H_2O	hexadecane	1.01	1.05
diethylamine·H_2O	diphenylmethane	0.85	1.01
diethylamine·H_2O	benzyl ether	0.80	0.90
diethylamine·CH_3OH	hexadecane	0.74	0.93
diethylamine·CH_3OH	diphenylmethane	0.73	0.89
diethylamine·CH_3OH	benzyl ether	0.70	0.85
benzene·I_2	CCl_4	1.0	0.8
diethyl ether·I_2	heptane	1.0	0.88
pyridine·I_2	a	-	0.93
trimethylamine·SO_2	heptane	1.30	1.21
trimethylamine·SO_2	chloroform	1.43	1.44
trimethylamine·SO_2	dichloromethane	1.62	1.51
m-F-phenol· dimethylsufoxide	b	0.58	-
m-F-phenol· ethylacetate	b	0.45	-

TABLE 1 Continued

Complex	Solvent	α	α'
m-F-phenol · pyridine	b	0.61	-
m-F-phenol · triethylamine	b	0.68	-
TCNE · triphenylene	c	-	0.65

a. Several nonpolar and slightly polar solvents.

b. Estimated from enthalpy data for several non-polar and slightly polar solvents; gas phase data not available.

c. Estimated from free energy data for several non-polar and slightly polar solvents; gas phase data not available.

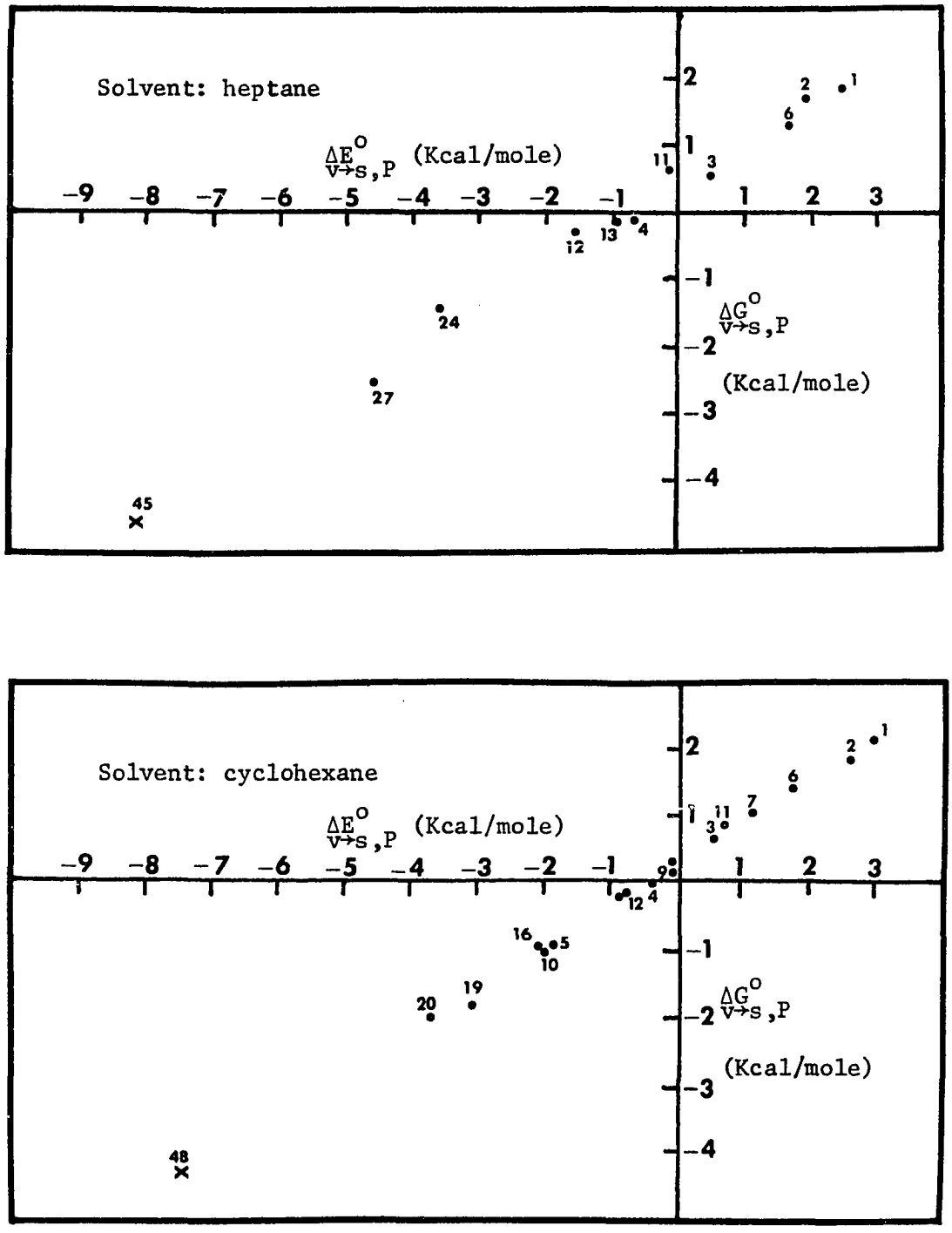


Figure 4: Correlation of energies and free energies of transfer of solutes from gas to solvents heptane and cyclohexane at 25°C.

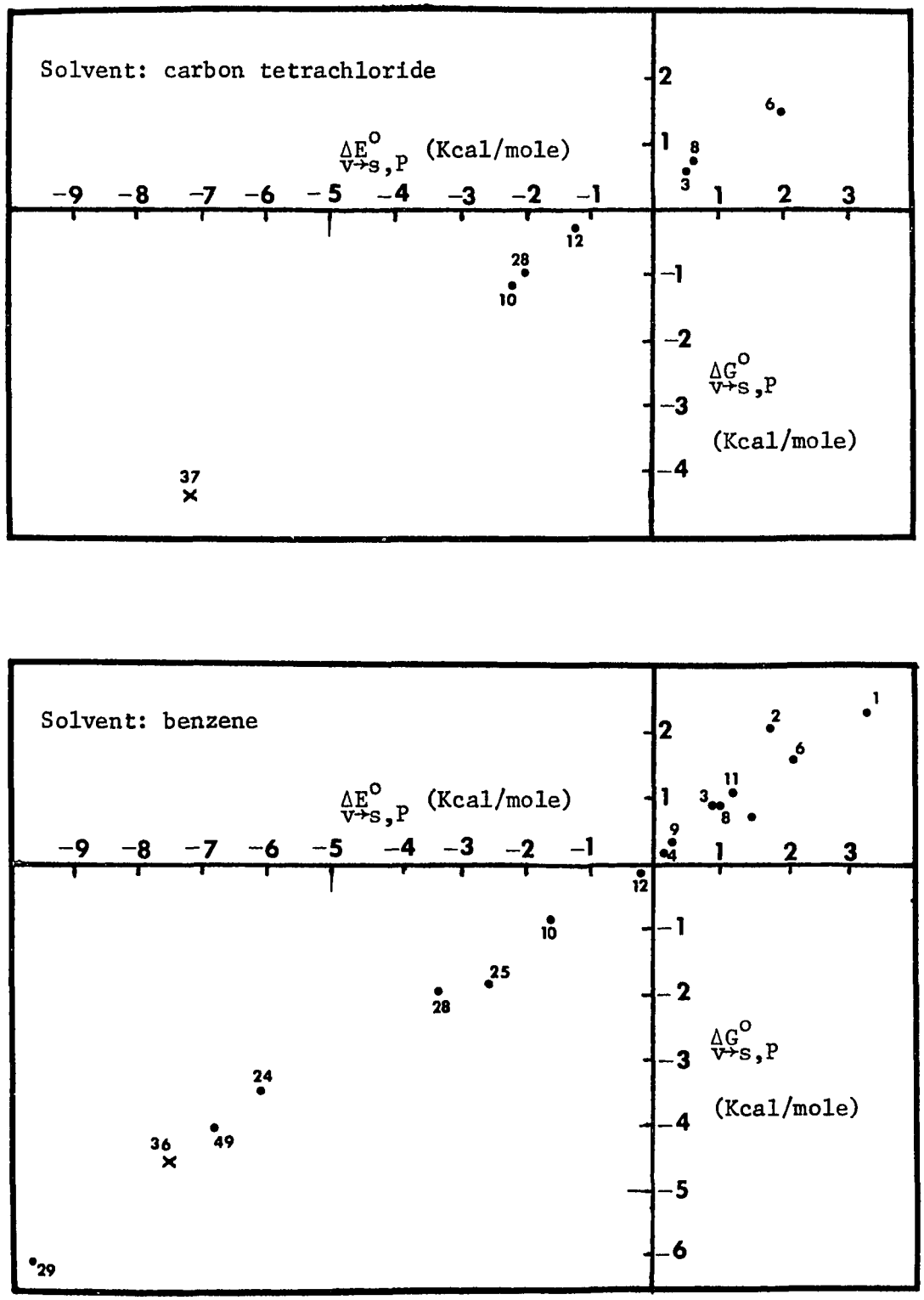


Figure 5: Correlation of energies and free energies of transfer of solutes from gas to solvents carbon tetrachloride and chloroform at 25°C.

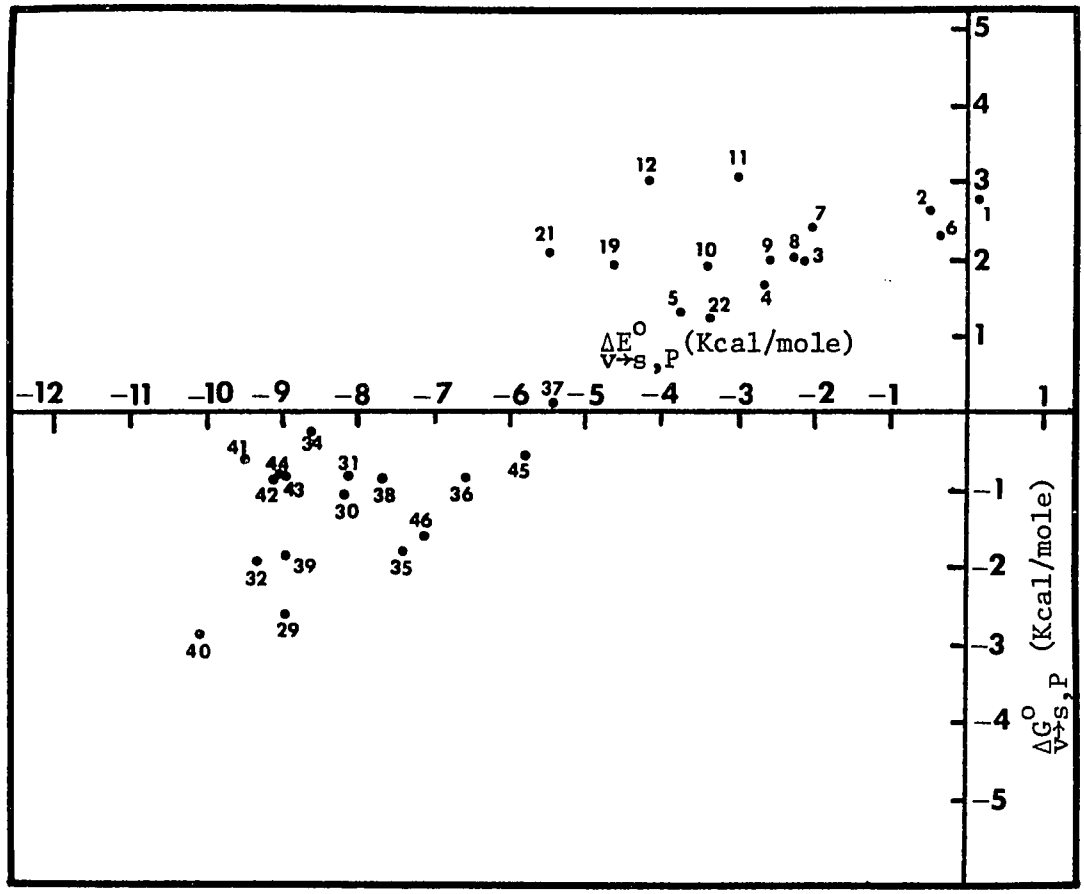


Figure 6: Correlation of energies and free energies of transfer of solutes from gas to water 25°C.

LEGEND FOR FIGURES 4-6

1, He; 2, Ne; 3, Ar; 4, Kr; 5, Xe; 6, H_2; 7, N_2: 8, O_2; 9, CH_4; 10, C_2H_6; 11, CF_4; 12, SF_6; 13, CO_2; 14,C_2F_6; 15, C_3F_8; 16, c-C_4F_8; 17, $CClF_3$; 18, NO; 19, C_3H_8; 20, c-C_3H_6; 21, n-C_4H_{10}; 22, C_2H_4; 23, CO; 24, SO_2; 25, C_2H_2; 26, Rn; 27, $(CH_3)_3N$; 28, H_2O; 29, I_2; 30, $CHCl_3$; 31, $CHCl_2CH_3$; 32, $CHCl_2CH_2Cl$; 33, CCl_3CH_2Cl; 34, CCl_3CH_3; 35, CH_2ClCH_2Cl; 36, C_6H_6; 37, CCl_4; 38, $C_6H_5CH_3$; 39, $C_{10}H_8$; 40, $(C_6H_5)_2$; 41, $C_6H_5(i\text{-}C_3H_7)$; 42, m-$C_6H_4(CH_3)_2$; 43, p-$C_6H_4(CH_3)_2$; 44, $C_6H_5C_2H_5$; 45, C_6H_5Cl; 46, o-$C_6H_4Cl_2$; 47, n-C_7H_{16}; 48, c-C_6H_{12}. × indicates the solvent itself.

Standard states of solutes are 1 molar, ideal dilute solution for vapor and condensed phases.

fore it is possible that $\Delta G^{o}_{v\to s,i}$ for the solvation process can be inferred from the corresponding $\Delta E^{o}_{v\to s,i}$ for practical purposes by equation 22.

Equation 22 leads to explanation of why α and α' values are nearly the same. When the expressions for $\Delta G^{o}_{v\to s,i}$ from equation 22 are substituted in the α' expression one obtains

$$\alpha' = \frac{\Delta G^{o}_{v\to s,DA}}{\Delta G^{o}_{v\to s,D} + \Delta G^{o}_{v\to s,A}}$$

$$\alpha' = \frac{\beta_s \Delta E^{o}_{v\to s,DA} + 300}{\beta_s \Delta E^{o}_{v\to s,D} + \beta_s \Delta E^{o}_{v\to s,A} + 600} \cong \frac{\Delta E^{o}_{v\to s,DA}}{\Delta E^{o}_{v\to s,D} + \Delta E^{o}_{v\to s,A}} = \alpha$$

Thus, since a few hundred calories are ordinarily negligible compared with the usual magnitude of several kilocalories for the $\Delta E^{o}_{v\to s,i}$ values for complexing species, α and α' should be nearly equal.

The preceding relationships show the utility of the important transfer energies and free energies ($\Delta E^{o}_{v\to s,i}$ and $\Delta G^{o}_{v\to s,i}$) in predicting solvent effects. It would seem desirable, therefore, to attempt to develop theoretical methods for predicting these quantities. The next chapter introduces a model developed in the course of this research for calculating $\Delta E^{o}_{v\to s,i}$ and $\Delta G^{o}_{v\to s,i}$ for polar as well as nonpolar solutes.

CHAPTER III

THE NONPOLAR ANALOG MODEL[152]

As extensive thermodynamic and spectral information about molecular complexes has become available, numerous investigators have noted the important role played by solvents in modifying the physical and chemical properties of complexes.[41-45,49] This knowledge has provided the incentive for attempts to obtain accurate experimental results for electron donor-acceptor (EDA) complexes in the vapor phase,[42,43,45,49] where the complicating effects of solvents are absent, and for which theoretical treatments of the structure and energy of complexes are becoming feasible. Unfortunately, limitations on the volatility and stability of EDA complexes and the unique experimental problems connected with investigations of associating gases have restricted the number and reliability of studies of gaseous complexes.[35,41-46,49]

There are two primary reasons, therefore, why methods for predicting the effects of media on complex formation reactions are potentially valuable: 1) comparison with theory will be facilitated if reliable techniques evolve for converting thermodynamic information about complex formation in condensed phases into information about the corresponding gaseous system; and 2) an understanding of the role of solvents in altering properties of complexes will be essential in future attempts to provide a molecular explanation of biological and industrial

systems in which EDA complexes are important.

Attempts to treat the influence of solvents on the energetics of complex formation have generally fallen into two classes--methods in which the solvent is treated as a chemical reactant, which forms discrete complexes with donor (D), acceptor (A) or the adduct (DA);[27,47,48,50] and techniques for inferring the effects of non-specific solvent-solute interactions.[16,17,36,45,51] Although it is clear that specific complexes between solvent and solute can be important in condensed phase systems of associating solutes, there appears to be no unique way to determine stoichiometries and specific thermodynamic constants for the solvent-solute complexes which are presumed to exist in dilute solution.[45,51] Progress has been made in predicting energies and free energies of transfer reactions of the type.

$$i\ (\text{ideal gas at unit molarity}) = i\ (\text{ideal dilute solution in solvent } \underline{S} \text{ at unit molarity}) \qquad (23)$$

for polar solutes involved in representative molecular complex formation reactions.[45,34,52,53]

The general problem of developing a theory of nonelectrolyte solutions involving polar components remains unsolved.[54] Attempts have been made to compare properties of solutions of polar solutes with those of homomorphic nonpolar solutes. Bondi and Simkin[55] introduced the concept of homomorph, where the hydroxyl group of alcohols was replaced by the methyl group while maintaining total dispersion forces to remain same, to evaluate the hydrogen-bond contribution of the heat of vaporization of liquid aliphatic alcohols. In their hydrogen-bond study by gas-liquid partition chromatography, Martire and Riedle[56]

employed a reference solvent which has identical molar volume and polarizability as electron donating solvents to differentiate the thermodynamic properties steming from the complexes formed between the solvents and the solutes. Estimates have been made of the separate contributions of dispersive and inductive interactions to the solubility parameters of polar liquids, and these parameters have found some utility in treatments of binary mixtures of polar and nonpolar compounds.[57,58] However, it is apparent that the total effect of interactions between polar and nonpolar molecules, throughout a wide range of concentrations, cannot be rigorously accounted for in terms of a single induction energy density parameter which is concentration independent.[54]

The transfer reactions (equation 23) for the components participating in a molecular complex formation reaction pertain to the formation of infinitely dilute solutions of polar solutes in a given solvent, S. For purposes of the present discussion, S will be taken to be nonpolar. Solute molecules are in contact only with solvent molecules, and the solvent-solute interactions involve only nonspecific dispersion and induction forces. Therefore, it should be much simpler to develop adequate theories for predicting transfer energies and free energies of polar solutes than to formulate theories of pure polar liquids and of concentrated solutions of polar and nonpolar molecules, in which orientation energy and entropy effects must be considered.

A general model for dilute solutions of polar compounds dissolved in nonpolar media is proposed. The model involves use of a nonpolar analog (NPA) of the polar solute (P) in place of the polar solute in calculating properties of the solutions; the NPA molecule is

chosen to have the same molecular volume and the same total interaction energy with the surrounding solvent molecules as does P. In this model, the NPA molecule must have a value of molecular polarizability, α_{NPA}, large enough to interact as strongly with the solvent as does P, for which both dispersion and inductive interactions are important. It is assumed that not only $\Delta E^{o}_{v\to s,P}$, but also $\Delta G^{o}_{v\to s,P}$, $\Delta S^{o}_{v\to s,P}$ and other thermodynamic constants will be the same as the corresponding transfer quantities for the NPA molecule. No attempt is made to utilize or predict properties of the pure polar component in this treatment. The theoretical basis for the NPA model and methods for applying it to predict the effects of solvents on molecular complex formation equilibria are presented here.

Theoretical Basis for the Nonpolar Analog Model

When an isolated polar molecule is dissolved in a non-polar medium there are several kinds of intermolecular interactions which occur between the solute and solvent molecules. These include the short range repulsive forces, and attractive forces such as the dipole-induced interaction and dispersive forces of the van der Waals type.[59,60] The potential energy of interaction between the polar molecule P and the solvent molecules S as a result of the dipole-induced dipole forces is

$$V_{ps}\ (\text{dip}) = -\frac{1}{2}\,\underset{\sim}{\mu}_{p} \cdot \underset{\wedge}{R}_{ps} \qquad (24)$$

Here $\underset{\wedge}{R}_{ps}$ is the reaction field at the polar molecule resulting from the polarization of the solvent molecules by the electric moment of

the solute molecule, $\underset{\sim}{\mu}_p$. At this point one may adopt the dielectric cavity model of a solution in which the solute molecule is assumed to sit at the center of a cavity whose walls consist of a continuum with dielectric properties identical with the bulk pure solvent. The reaction field is then proportional to the electric moment; the coefficient of proportionality is given in several standard texts on dielectric theory.[59] Since a numerical value of the potential energy of interaction is not required here, the reaction field will instead be written as a summation over the contributions of each solvent-solute pair,

$$V_{ps}(\text{dip}) = -\frac{1}{2}\mu_p^2 \sum_s \frac{\alpha_s f_{ps}}{|\underset{\sim}{r}_{ps}|^6} \tag{25}$$

where $|\underset{\sim}{r}_{ps}|$ is the magnitude of the vector distance between a solvent molecule and the polar molecule, α_s is the molecular polizability of a solvent molecule, and f_{ps} is an orientation factor which accounts for the anisotropy of the interactions. The dispersive interaction may be written as

$$V_{ps}(\text{disp}) = -\frac{3}{2} I_p \alpha_p \sum_s \frac{I_s \alpha_s}{I_p + I_s} \frac{1}{|\underset{\sim}{r}_{ps}|^6} \tag{26}$$

where I_p and I_s are the ionization potentials of the solute and solvent, respectively, and α_p is the molecular polarizability of the solute.

The NPA molecule has no permanent dipole moment; it interacts with the solvent molecules solely through dispersive forces. However, the magnitude of this interaction must be large enough so that

the total energy of interaction of the NPA molecule with the solvent

$$V_{NPA} = -\frac{3}{2} I_{NPA}\, \alpha_{NPA} \sum_s \frac{I_s\, \alpha_s}{I_{NPA} + I_s} \frac{1}{|r_{NPA-s}|^6} \qquad (27)$$

equals the total energy of interaction of the original polar molecule with the solvent (the sum of equations 25 and 26):

$$V_{NPA} = V_{ps}(dip) + V_{ps}(disp) \qquad (28)$$

Hypothetically, the energy compensation required by equation 28 may be considered to occur in the following way. Imagine that the electric moment, μ, of the polar molecule is "switched off" and that concomitantly the molecular polarizability and/or ionization potential of P are incremented to the new values α_{NPA} and I_{NPA}, which are chosen to ensure equivalence of the NPA-solvent and P-solvent interaction energies. Since all of the terms in the sums in equation 28 have the same distance dependence, they can be equated term by term so that for each solute-solvent interaction

$$-\frac{3}{2} I_{NPA}\, \alpha_{NPA} \frac{I_s\, \alpha_s}{I_{NPA} + I_s} = -\frac{1}{2} \mu_p^2\, \alpha_s\, f_{ps} - \frac{3}{2} I_p\, \alpha_p \frac{I_s\, \alpha_s}{I_p + I_s} \qquad (29)$$

As an example of how the compensation may be effected, consider a situation in which the solvent polarizability is spherical and where the energy equality required by equation 28 is to be achieved by varying only the molecular polarizability of the solute, while leaving the ionization potential invariant. Then, equation 29 may be solved for α_{NPA} to yield

$$\alpha_{NPA} = \alpha_p + \frac{1}{3} \frac{I_p + I_s}{I_p I_s} \mu_p^2 \qquad (30)$$

where f_{ps} has been taken to be equal to unity.

Note that any other combination of values of I_{NPA} and α_{NPA} which satisfy equation 29 may be chosen for the hypot hetical solute molecule NPA.

The crucial question here concerns the change in $\Delta S^o_{v \to s,i}$ in transforming the polar solute into the NPA analog. To examine this question, the simple cell model of a liquid introduced by Lennard-Jones and Devonshire[61,62] will be adopted to describe the thermodynamics of the polar molecule NPA molecule transformation in solution. In this treatment, each solute and solvent molecule occupies a "cell"; the dynamics of an individual solute molecule, which is surrounded entirely by solvent molecules, is treated as independent of the dynamics of all other molecules. The Helmholtz free energy of the solute molecule in the cell is

$$A = - NkT \ln \frac{v_f(v,T)e}{\Lambda^3} + \frac{N \Phi (0; v)}{2} \qquad (31)$$

Here, N is the number of cells in a volume V of the liquid, v = V/N, k is the Boltzman constant, and

$$\Lambda = \frac{h}{(2\pi mkT)} \qquad (32)$$

where m is the mass of the solute and h is Planck's constant. In equation 31 $v_f(v,T)$ is the effective volume of the cell in which the

solute molecule can move,

$$v_f(v, T) = \int_{cell} e^{-\Psi(r)/kT} 4\pi r^2 \, dr \tag{33}$$

and

$$\Psi(r) = \Phi(r) - \Phi(0) \tag{34}$$

where $\Phi(r)$ is the potential energy of interaction of the solute molecule which is at some distance r from the center of the cell. From the definition $S = -\left(\frac{\partial A}{\partial T}\right)_{V, N}$, the entropy of the solute in the cell defined by neighboring solvent molecules is

$$S = NK \ln \frac{v_f e}{\Lambda^3} \frac{5}{2} + \frac{NkT}{v_f} \left(\frac{\partial v_f}{\partial T}\right)_v \tag{35}$$

In the cell model of a liquid there is no change in the entropy of the system as the polar solute molecule is changed to the NPA molecule; this follows from inspection of equations 33-35 and 29. The entropy of the solute molecule is a function of the volume of the cell and the free energy of interaction, $\Psi(r)$. The non-polar analog has been chosen so as to have the same molecular volume and the same free energy of interaction with the solvent as the polar solute molecule. This implies that the volume of the cell and the effective cell volume will remain unchanged. The entropy of the remaining molecules in the solvent is unchanged since the cage containing the NPA molecule interacts with the rest of the system in exactly the same manner as does the polar molecule. There is no net ordering effect of the polar molecule

on the non-polar solvent since dipole-induced dipole potential energies of interaction are always at the minimum of the interaction configuration; in other words the induced dipoles of the individual solvent molecules always lie in the direction of the dipole of the polar solute molecule and instantaneously follows the various orientations of the solute molecule (neglecting retardation effects).

Obviously, more elaborate cell theories (in which the potential energy of interaction between solute and solvent is taken to be non-spherical) will also be consistent with the NPA model, provided the compensation of solute-solvent interaction energy terms is properly accomplished. Equation 29 must be satisfied for each volume element of the NPA and P molecules, which for convenience may be taken to have identical molecular geometries. In place of each dipolar contribution given by equation 25 there will be an equivalent energy term given by equation 27 for the nonpolar analog molecule. No matter how complicated the polar solute may be, the elements of interaction of P with S may be mapped in a one-to-one way into equivalent NPA-S interactions, all of which are of the dispersive type. The equality of all thermodynamic functions for the transfer reactions P (ideal gas) → P (ideal dilute solution in S) and NPA (ideal gas) → NPA (ideal dilute solution in S) is thus ensured.

Application of the Nonpolar Analog Model in Predicting Thermodynamic Properties of Polar Solutes

The NPA model does not by itself provide a basis for predicting thermodynamic properties for the transfer reactions (equation 23) for

polar solutes. However, to the extent that the model applies it permits the use of theories and properties of nonpolar liquids and liquid mixtures in predicting properties of dilute solutions of polar solutes in nonpolar solvents. The model is based on the assumption that $\Delta G^{o}_{v\to s,P}$ is uniquely determined by $\Delta E^{o}_{v\to s,P}$ and the molecular volume (more correctly, the molecular geometry) of P. Using the nonpolar analog concept,

$$\Delta G^{o}_{v\to s,P}\ (\Delta E^{o}_{v\to s,P},\ \bar{V}_{P}) = \Delta G^{o}_{v\to s,NPA}\ (\Delta E^{o}_{v\to s,NPA},\ \bar{V}_{NPA}) \qquad (36)$$

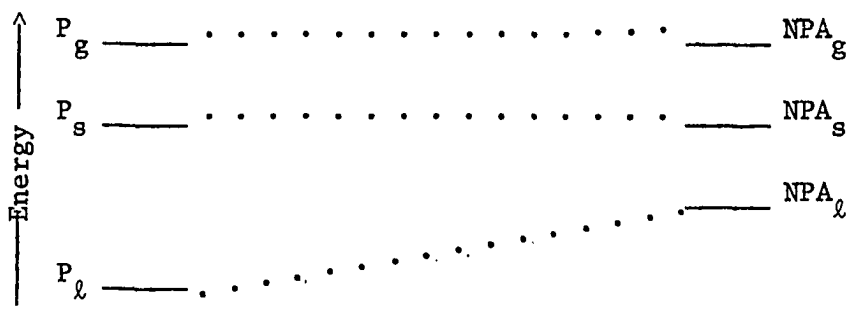
where

$$\Delta E^{o}_{v\to s,P} \equiv \Delta E^{o}_{v\to s,NPA} \text{ and } \bar{V}_{P} \equiv \bar{V}_{NPA}\ .$$

The NPA model may be most simply tested by comparing experimental values of $\Delta G^{o}_{v\to s,i}$ and $\Delta E^{o}_{v\to s,i}$ for various solutes i (polar and nonpolar) of comparable molecular volume dissolved in a given solvent. The linear correlationship between $\Delta E^{o}_{v\to s,i}$ and $\Delta G^{o}_{v\to s,i}$ of the equation 22 demonstrates the feasibility of replacing P by its nonpolar analog in thermodynamic calculations; it is also shown that moderate variation in molecular volume does not strongly influence the magnitude of $\Delta G^{o}_{v\to s,i}$ corresponding to a given value of $\Delta E^{o}_{v\to s,i}$. Actually, there is a reasonably close correlation between $\Delta E^{o}_{v\to s,i}$ and the molecular volume of related solutes; hence, the effect of variation in solute volume is largely hidden in the $\Delta G^{o}_{v\to s,i}$ vs. $\Delta E^{o}_{v\to s,i}$ correlations. Therefore, the molecular volume of the pure P instead of its actual partial volume in the dilute solutions is used for the molecular volume of the NPA molecules without

causing significantly different results in the calculated $\Delta G^{o}_{v\to s,i}$ values by this model from the experimental $\Delta E^{o}_{v\to s,i}$ values.

At a more fundamental level, it would be desirable to develop theories for predicting $\Delta E^{o}_{v\to s,P}$ and $\Delta G^{o}_{v\to s,P}$ from molecular parameters of the P, S and NPA molecules. In this development, it is convenient to refer to the following conceptual diagram of the energy of P and NPA in various states:



The states P_g and NPA_g refer to ideal gaseous states; P_s and NPA_s refer to dilute solution states in the nonpolar solvent; and P_ℓ and NPA_ℓ represent pure liquid P and NPA. Gaseous standard states are taken to be the unit molarity ideal gas and the infinitely dilute, unit molarity state is used for all solutes in condensed phase. Note that the energy of P_ℓ will ordinarily be considerably lower than that of NPA_ℓ and that the energy change for the transfer $P_\ell \to P_s$ will be correspondingly greater than that for the transfer $NPA_\ell \to NPA_s$; the reason for this is that in the pure liquid state, P molecules interact relatively strongly with each other through orientation forces, which are absent in liquid NPA and in the states P_s and NPA_s. The model forces P_g and NPA_g to be at the same level of energy (and by assumption, free energy);

similaryly, P_s and NPA_s have the same energy (and, presumably, free energy).

Given the energy level diagram above, the NPA model requires that

$$\Delta E^{o}_{v\rightarrow s,P} = \Delta E^{o}_{v\rightarrow s,NPA} = E^{o}_{NPA_s} - E^{o}_{NPA_g} \tag{37}$$

or

$$\Delta E^{o}_{v\rightarrow s,P} = (E^{o}_{NPA_s} - E^{o}_{NPA_\ell}) - (E^{o}_{NPA_g} - E^{o}_{NPA_\ell}) \tag{38}$$

and similarly

$$\Delta G^{o}_{v\rightarrow s,P} = (G^{o}_{NPA_s} - G^{o}_{NPA_\ell}) - (G^{o}_{NPA_g} - G^{o}_{NPA_\ell}) \ . \tag{39}$$

Equations 38 and 39 may be rewritten

$$\Delta E^{o}_{v\rightarrow s,P} = \Delta E^{o\,dil}_{NPA} - \Delta E^{o\,vap}_{NPA} \tag{40}$$

and

$$\Delta G^{o}_{v\rightarrow s,P} = \Delta G^{o\,dil}_{NPA} - \Delta G^{o\,vap}_{NPA} \tag{41}$$

where $\Delta E^{o\,dil}_{NPA}$ and $\Delta E^{o\,vap}_{NPA}$ are, respectively, the energy of transfer of NPA from pure liquid NPA into the infinitely dilute solution state in solvent S and the energy of vaporization of liquid NPA, and $\Delta G^{o\,dil}_{NPA}$ and $\Delta G^{o\,vap}_{NPA}$ are the corresponding free energy changes.

Several current theories of solution provide means for relating $\Delta E^{o\,dil}_{NPA}$ and $\Delta E^{o\,vap}_{NPA}$ to parameters characteristic of the NPA and S molecules. For example, solubility parameter theory[54] predicts that

$$\Delta E^{o\,dil}_{NPA} = \bar{V}_P(\delta_S - \delta_{NPA})^2 \tag{42}$$

and

$$\Delta E^{o\,vap}_{NPA} = \delta^2_{NPA}\,\bar{V}_P \qquad (43)$$

where δ_S and δ_{NPA} are the solubility parameters of S and NPA, respectively, and where for convenience we neglect volume changes on mixing NPA with S. The expressions for $\Delta E^{o\,dil}_{NPA}$ and $\Delta E^{o\,vap}_{NPA}$ in equations 42 and 43 may be substituted into equation 40, which may be rearranged to give

$$\delta_{NPA} = \frac{1}{2}\left(\delta_S - \Delta E^o_{v\to s,P}/\delta_S\bar{V}_P\right) . \qquad (44)$$

Thus, it is possible to infer the solubility parameter of the nonpolar analog of a given polar solute from the solubility parameter of the solvent and the energy of transfer of P from the ideal gaseous state into the infinitiely dilute state in S. The free energy of transfer of NPA from vapor to the infinitely dilute state in solvent S may then be related to δ_{NPA} and the vapor pressure of pure liquid NPA (P^o_{NPA}). Equation 39 may be rewritten

$$\Delta G^o_{v\to s,P} = RT\ell n(P^o_{NPA}/RT) + \bar{V}_P(\delta_S - \delta_{NPA})^2 + RT\ell n\bar{V}_S \qquad (45)$$

where the first term on the right represents the free energy change for converting NPA vapor at unit molarity into pure liquid NPA under its own vapor pressure; the second term is the free energy of transfer of NPA from the pure liquid state to the ideal dilute solution of S (using the unit mole fraction standard state) and the last term is the free energy change for converting from the mole fraction standard state for the solute to the unit molarity standard state.

In order to apply equation 45 to calculate $\Delta G^{o}_{v\rightarrow s,P}$ it is necessary to obtain the vapor pressure of pure liquid NPA, either from a theory of pure liquids or from experimental measurements on actual nonpolar liquids having approximately the required heat of vaporization and molecular geometry. Fortunately, the vapor pressures of pure low molecular weight nonpolar liquids at 25° vary systematically with their energies of vaporization.[63] Figure 7 is a plot of the logarithm of vapor pressure against $(\Delta E^{o\,vap}_{298})^{1.15}$ for a number of common nonpolar liquids (excluding fluorocarbons); the solid curve represents the least squares equation

$$\log_{10} P^{o}(\text{torr, } 298^{o}K) = -1.038\text{x}10^{-4}\ (\Delta E^{o\,vap}_{298})^{1.15} + 4.889 \qquad (46)$$

which may be used to calculate vapor pressures of these liquids, with a standard error of about 9%.[64] (Prediction of vapor pressures of nonpolar liquids at different temperatures is discussed in the Appendix II.) By employing $\Delta E^{o\,vap}_{NPA} = \delta^{2}_{NPA}\,\overline{V}_{P}$ and equation 46 it is possible to obtain a reliable value P^{o}_{NPA} to use in equation 45.

Another theory of solutions which may be melded with the NPA model is the average-potential cell model theory of Prigogine,[65] which extends the theorem of corresponding states to mixtures. In the Prigogine refined average-potential cell model, excess thermodynamic functions for binary mixtures are expressed in terms of parameters σ and ρ defined as

$$\sigma = \frac{\varepsilon^{*}_{B} - \varepsilon^{*}_{A}}{\varepsilon^{*}_{A}} \qquad (47)$$

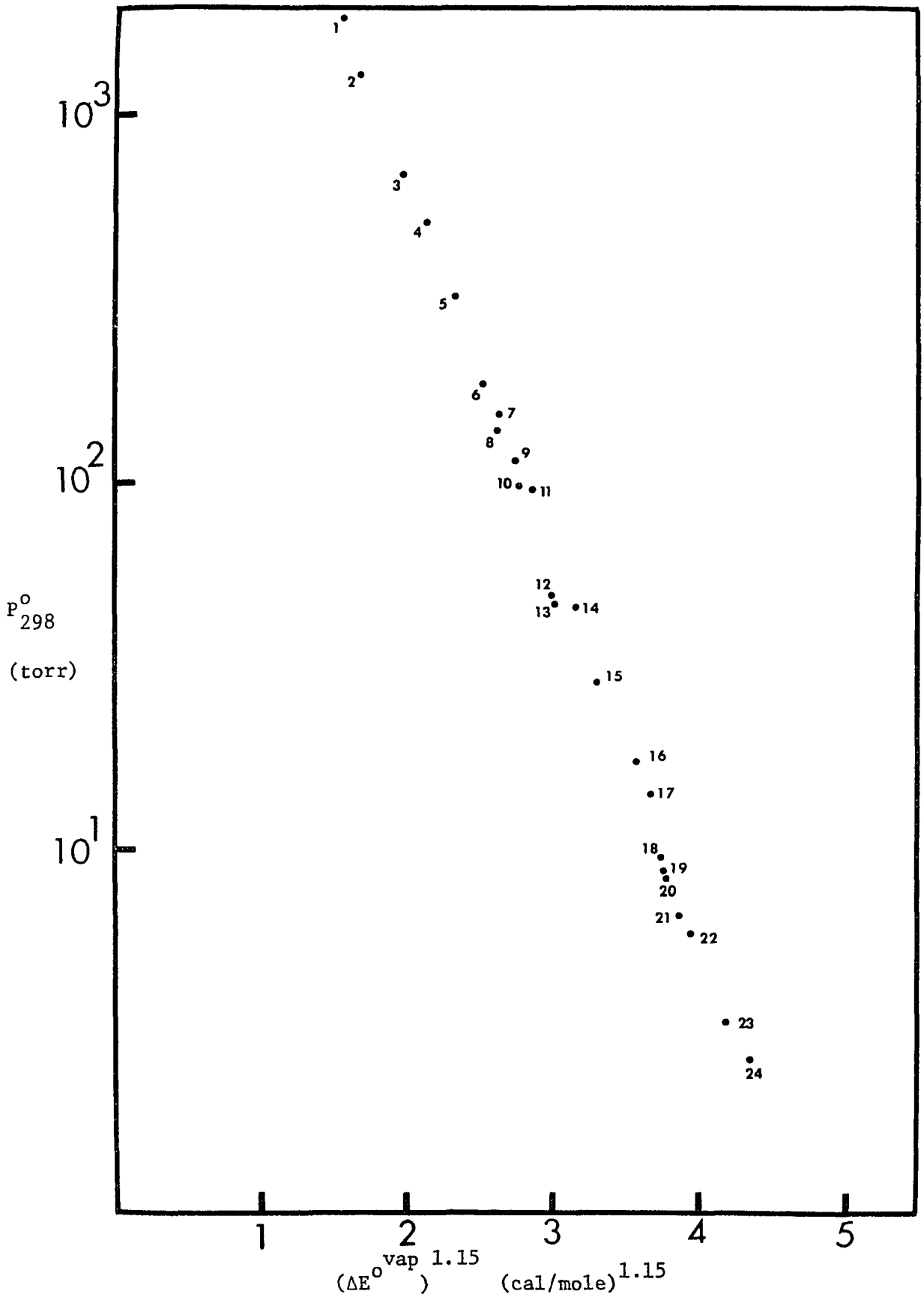


Figure 7: Correlation of vapor pressure and energy of vaporization at 25°C.

LEGEND FOR FIGURE 7

1, butane; 2, neopentane; 3, isopentane; 4, pentane; 5, cyclopentane; 6, 1-hexene; 7, hexane; 8, methylcyclopentane; 9, carbon tetrachloride; 10, cyclohexane; 11, benzene; 12, isooctane; 13, methylcyclohexane; 14, heptane; 15, toluene; 16, 1-octene; 17, octane; 18, ethylbenzene; 19, p-xylene; 20, m-xylene; 21, o-xylene; 22,stylene; 23, propylbenzene; 24, mesitylene.

Values of vapor pressure are from reference 128.

and

$$\rho = \frac{\gamma_B^* - \gamma_A^*}{\gamma_A^*} \tag{48}$$

where γ^* and ε^* are the distance of separation and internal energy scale factors in the universal potential function, respectively, and the subscripts A and B denote pure components A and B, respectively. Here, A is taken to be the reference compenent. When only dispersion forces operate between the two components (which is the case when the solute is the NPA molecule), $\Delta E^{o\,dil}$ and $\Delta G^{o\,dil}$ may be expressed as

$$\Delta E^{o\,dil} = [-\frac{1}{4} H_A^o + \frac{T}{4} C_{p_A} - \frac{1}{8} T^2 (4C'_{p_A} - C'_{v_A})] \sigma^2 + (-9H_A^o + 9TC_{p_A}) \rho^2 \tag{49}$$

and

$$\Delta G^{o\,dil} = [-\frac{1}{4} H_A^o + \frac{T}{8} (4C_{p_A} - C_{v_A})] \sigma^2 + (-9H_A^o - \frac{15}{2} RT) \rho^2 - \frac{3}{4} RT \sigma\rho \tag{50}$$

where H^o is the configurational enthalpy, C_p and C_v are configurational molar heat capacities at constant pressure and volume, respectively, and C'_p and C'_v are the first derivatives of the configurational molar heat capacities with respect to T. The $\Delta E^{o\,dil}$ and $\Delta G^{o\,dil}$ expressions given above are, strictly speaking, valid only at zero pressure. However at applications involving pressures not greater than one atmosphere, the pressure dependence of energy or free energy may ordinarily be ignored. The parameter ρ should be evaluated from the critical volumes of A and B, but for the present calculations it is satisfactory to estimate ρ

from the molar volumes of A and B at 298°K.

The relations

$$\Delta H^{o\,vap} = 0.678\ Z\ \varepsilon_A^*/RT \tag{51}$$

and

$$\varepsilon_B^* = \varepsilon_A^*\ (1 + \sigma) \tag{52}$$

where Z is the number of the nearest neighbors surrounding a cell, may be combined with equations 40 and 41 to give

$$\Delta E^o_{v\to s,P} = [-\frac{1}{4} H_A^o + \frac{T}{4} C_{p_A} - \frac{1}{8} T^2\ (4C'_{p_A} - C'_{v_A})]\ \sigma^2_{NPA} + (-9H_A^o + 9TC_{p_A})\ \rho^2$$

$$-\Delta H_A^{o\,vap}\ (1 + \sigma_{NPA}) + RT \tag{53}$$

and

$$\Delta G^o_{v\to s,P} = RT\ \ell n\ \frac{P^o_{NPA}\bar{V}_S}{RT} + [-\frac{1}{4} H_A^o + \frac{T}{8}\ (4C_{p_A} - C_{v_A})]\ \sigma^2_{NPA} + (-9H_A^o - \frac{15}{2} RT)\ \rho^2$$

$$-\frac{3}{4} RT\ \sigma_{NPA}\ \rho \tag{54}$$

where $\Delta H^{o\,vap}$ is the enthalpy of vaporization. Here Z for the pure reference component A is assumed to be the same as for the pure NPA molecules.

To relate $\Delta E^o_{v\to s,P}$ and $\Delta G^o_{v\to s,P}$, σ_{NPA} may be calculated from the equation 53 for a given value of $\Delta E^o_{v\to s,P}$ and a chosen value of ρ, whereupon σ_{NPA} and ρ may be substituted into the equation 54 to calculate $\Delta G^o_{v\to s,P}$. The parameter ρ may be evaluated from molecular volumes of the solute and the solvent. An alternative procedure is to construct a set of

TABLE 2

THEMODYNAMIC PROPERTIES USED IN CALCULATION OF $\Delta E^{o\,dil}$ and $\Delta G^{o\,dil}$

ACCORDING TO PRIGOGINE'S REFINED AVERAGE POTENTIAL MODEL. t=25°C

Solvent A	$H_A^{o\,vap}$ (cal/mole)	H_A^o (cal/mole)	C_{p_A} (cal/mole-°K)	C_{v_A} (cal/mole-°K)	C'_{p_A} (cal/mole-°K^2)	C'_{v_A} (cal/mole-°K^2)
heptane	8735	-8143	14.3	4.10	-0.0179	-0.0296
benzene	8090	-7498	14.8	4.98	-0.048	-0.038
carbontetra-chloride	7753	-7161	13.6	3.83	-0.009	-0.009
chloroform	7304	-6712	13.5	4.47	-0.0024	-0.0119
diethylether	6508	-5916	15.6	4.47	$-6.8 \cdot 10^{-4}$	$-2.1 \cdot 10^{-4}$
acetone	7666	-7074	14.8	5.70	-0.0220	-0.0216

plots of $\Delta G^{o}_{v\to s,P}$ vs. $\Delta E^{o}_{v\to s,P}$ by applying equations 53 and 54 with arbitrarily chosen σ values and a fixed value of ρ. Knowing ρ, for a given solute and solvent, $\Delta G^{o}_{v\to s,P}$ is estimated from the curve corresponding most nearly to the correct ρ value. Figures 8, 9, and 10 show standard $\Delta G^{o}_{v\to s,P}$ vs. $\Delta E^{o}_{v\to s,P}$ curves for different ρ values for the solvents heptane, benzene, carbontetrachloride, chloroform, acetone, and ether. As is shown for the solvent heptane in Figure 8, where a comparison is made between calculated $\Delta G^{o}_{v\to s,i}$ values based upon the average potential model of Prigogine and upon the solubility parameter theory, the predictions based on the two theories are seen to be nearly the same. Moreover, the results in Figures 8, 9, and 10 are in reasonable agreement with transfer free energy values calculated from the empirical equation 22. Thermodynamic properties used for calculation by Prigogine's theory are listed in Table 2.

In applying equations 49 and 50 it must be remembered that the theory is appicalbe only for small values of ρ.[65] For heptane as the solvent, the calculated intercept ($\Delta G^{o}_{v\to s,P}$ corresponding to $\Delta E^{o}_{v\to s,P} = 0$) equals 241 cal. from equation 45 and 284 cal. from equation 54, using $\rho = -0.27$ and physical properties of heptane at 298°K. The value $\rho = -0.27$ is computed using a solute molar volume intermediate between those of Ar and Kr, for which $\Delta E^{o}_{v\to heptane}$ is nearly zero at 298°K.

Column 5 of Table 3 lists values of $-\Delta G^{o}_{v\to s,P}$ calculated using equations 43-46, which are based on the NPA model and solubility parameter theory. Column 4 give $-\Delta E^{o}_{v\to s,P}$ values calculated with the quasi-lattice model of Stevens, et al.,[31,32,40] which utilizes energy parameters characteristic of interactions between specific atomic and submolecular groups of the solute and solvent molecules. In the 6th column are listed values of $-\Delta G^{o}_{v\to s,P}$ computed from equations 43-46, using

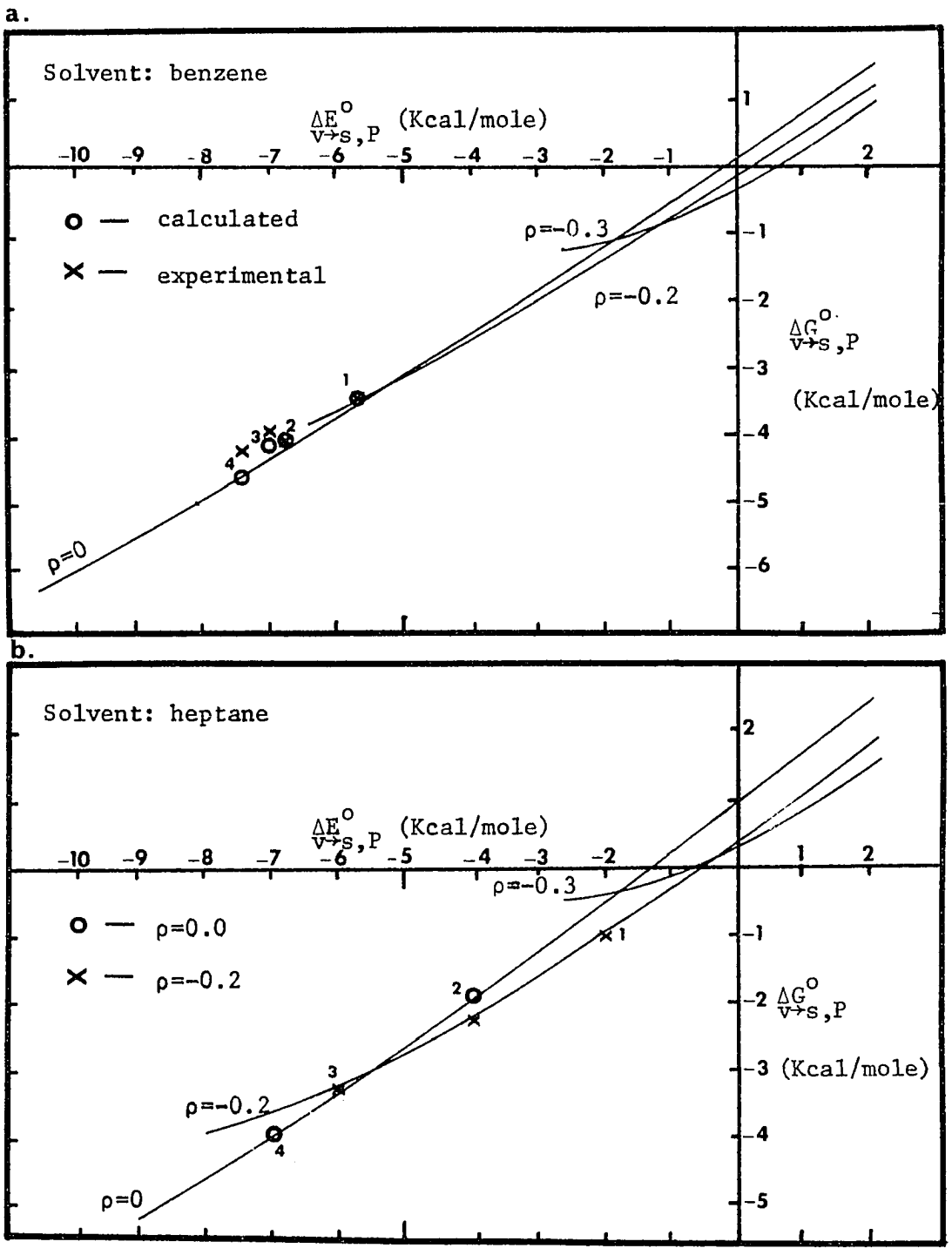


Figure 8: Standard $\Delta G^{o}_{v\to s,P}$ vs. $\Delta E^{o}_{v\to s,P}$ curves for different ρ values for solvents benzene and heptane at 25°C.

LEGEND FOR FIGURE 8

Figure 8a: Points ○ are calculated from the average potential cell model for some solutes using proper ρ values: points × are experimental.

1, cyclopentane; 2, cyclohexane; 3, isooctane;

4, heptane.

Figure 8b: Points ○ are calculated from the solubility parameter theory for hypothetical solutes whose molecular sizes correspon to ρ=0: points × are calculated in the same way using ρ=-0.2.

1, $\Delta E^{o}_{v\to s,P}$ = -2 Kca /mole; 2, $\Delta E^{o}_{v\to s,P}$ = -4 Kcal/mole;

3, $\Delta E^{o}_{v\to s,P}$ = -6 Kcal/mole; 4, $\Delta E^{o}_{v\to s,P}$ = -7 Kcal/mole.

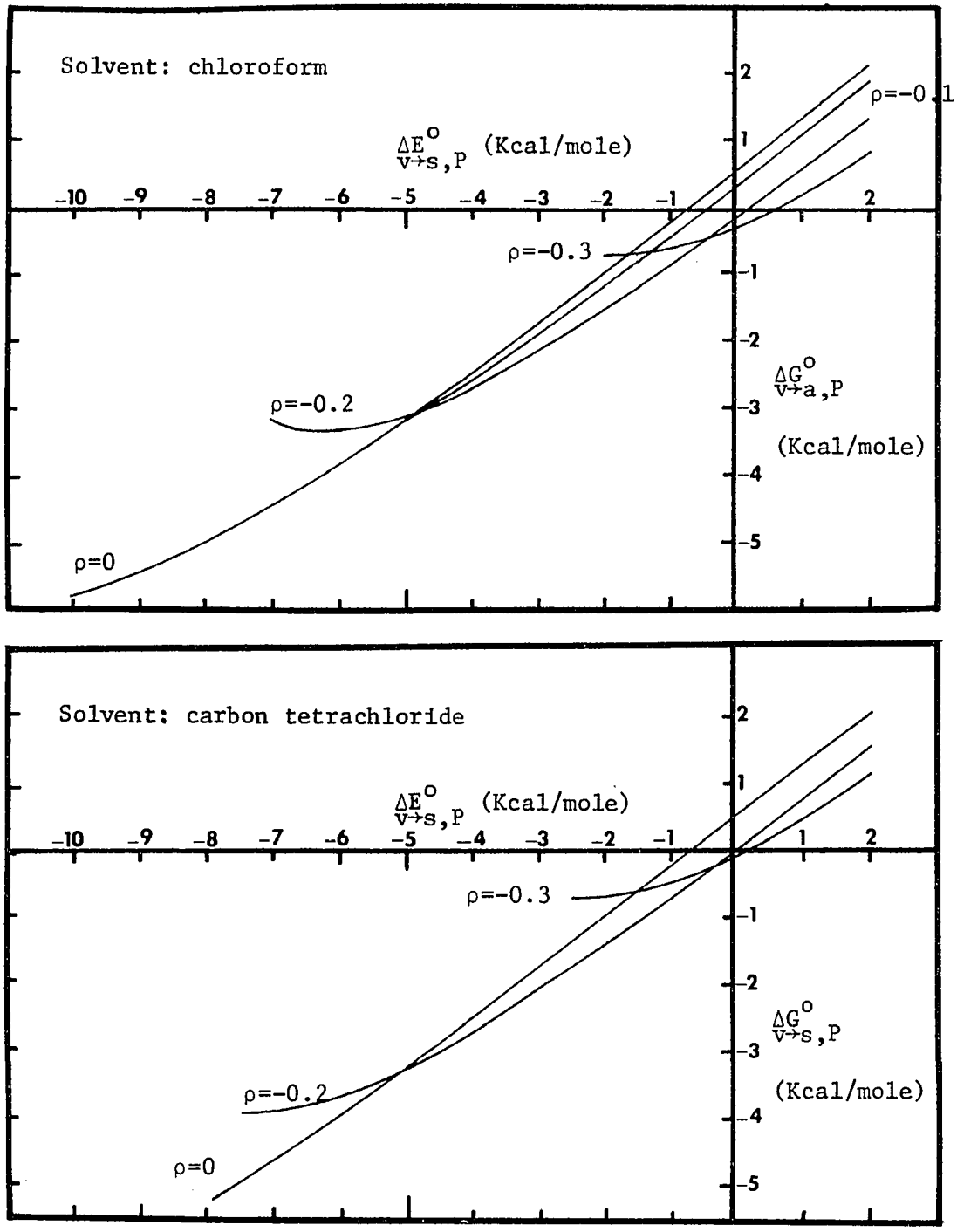


Figure 9: Standard $\Delta G^{o}_{v\to s,P}$ vs. $\Delta E^{o}_{v\to s,P}$ curves for different ρ values for solvents chloroform and carbon tetrachloride at 25°C.

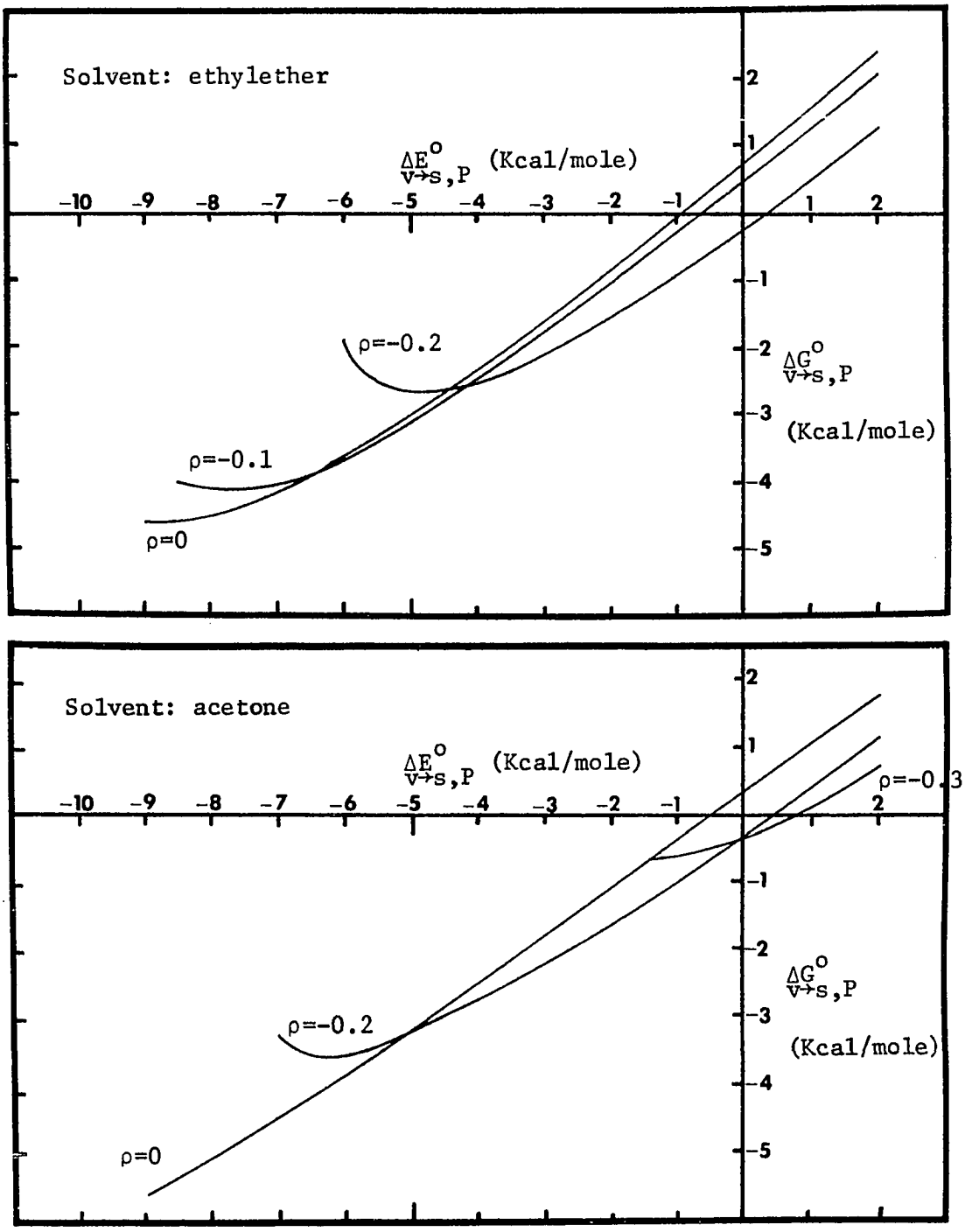


Figure 10: Standard $\Delta G^{o}_{v\to s,P}$ vs. $\Delta E^{o}_{v\to s,P}$ curves for different ρ values for solvents diethylether and acetone at 25°C.

TABLE 3

EXPERIMENTAL AND CALCULATED TRANSFER ENERGIES AND FREE ENERGIES

OF POLAR SOLUTES FROM VAPOR INTO NONPOLAR SOLVENT. t=25°C

Solute (P)	Solvent (S)[a]	$-\Delta E^{o}_{v\to s,P}$ (exptl.) (Kcal/mole)	$-\Delta E^{o}_{v\to s,P}$ (calcd.)[b] (Kcal/mole)	$-\Delta G^{o}_{v\to s,P}$ (calcd.)[c] (Kcal/mole)	$-\Delta G^{o}_{v\to s,P}$ (calcd.)[d] (Kcal/mole)	$-\Delta G^{o}_{v\to s,P}$ (exptl.) (Kcal/mole)
H_2O	HXD	1.98[33]	2.60	0.72	0.87	0.45[33]
methanol	HXD	2.75[33]	2.80	1.16	1.19	1.25[33]
diethylamine	HXD	5.45[33]	(5.45)[e]	2.66	(2.66)	3.16[33]
diethylamine·H_2O	HXD	7.50[33]	6.80	3.93	3.49	3.80[33]
diethylamine·methanol	HXD	5.98[33]	7.00	2.89	3.57	4.15[33]
H_2O	DPM	4.02[33]	5.57	1.89	2.19	1.79[33]
methanol	DPM	5.11[33]	4.78	2.79	2.62	2.34[33]
diethylamine	DPM	6.14[33]	(6.14)[e]	3.27	(3.27)	3.36[33]
diethylamine·H_2O	DPM	8.62[33]	8.26	4.88	4.63	5.20[33]
diethylamine·methanol	DPM	8.11[33]	7.46	4.40	4.38	5.08[33]

TABLE 3 continued

Solute (P)	Solvent (S)[a]	$-\Delta E^{o}_{v\to s,P}$ (exptl.) (Kcal/mole)	$-\Delta E^{o}_{v\to s,P}$ (calcd.)[b] (Kcal/mole)	$-\Delta G^{o}_{v\to s,P}$ (calcd.)[c] (Kcal/mole)	$-\Delta G^{o}_{v\to s,P}$ (calcd.)[d] (Kcal/mole)	$-\Delta G^{o}_{v\to s,P}$ (exptl.) (Kcal/mole)
trimethylamine	HPT	4.60[30]		2.60		2.57[30]
SO_2	HPT	3.60[30]		1.98		1.40[30]
trimethylamine·SO_2	HPT	10.10[30]		5.92		5.15[30]
CF_3COOH	CHX	2.1[31]		1.43		2.04[31]
CF_3COOH	CCl_4	3.2[31]		1.89		2.50[31]
CF_3COOH	C_6H_6	5.0[31]		3.09		3.76[31]
$(CF_3COOH)_2$	CHX	3.0[31]		1.32		2.08[31]
$(CF_3COOH)_2$	CCl_4	3.8[31]		1.89		2.79[31]
$(CF_3COOH)_2$	C_6H_6	4.3[31]		2.30		2.98[31]

[a] HXD=hexadecane, DPM=diphenylmethane, HPT=heptane, CHX=cyclohexane;

[b] Calculated from the lattice model of Stevens, et al.;

[c] Calculated from experimental $\Delta E^{o}_{v\to s,P}$ values, using the NPA model and solubility parameter theory;

TABLE 3 continued

[d] Calculated from $\Delta E^{o}_{v \rightarrow s,P}$ values derived from the lattice model, using the NPA method in conjunction with solubility parameter theory;

[e] Experimental $\Delta E^{o}_{v \rightarrow s,P}$ for diethylamine used in calculating lattice parameters for N···HXD and N···DPM interaction energy.

the calculated values of $\Delta E^{o}_{v\to s,P}$ listed in column 4. Both sets of calculated $\Delta G^{o}_{v\to s,P}$ values are in reasonable agreement with the experimental results, and there is apparently nearly random deviation on the order of several tenths Kcal between the experimental and calculated free energy values. In Figure 11, the calculated $\Delta G^{o}_{v\to s,P}$ values along with the experimental values are plotted against $\Delta E^{o}_{v\to s,P}$ from the data of Table 3.

A related useful application of the nonpolar analog model is the calculation of limiting activity coefficients of polar solutes (P) in nonpolar solvents, based on the pure liquid P standard state. $\Delta G^{o}_{v\to s,P}$ for the unit molarity solute state in S may be calculated for polar solutes from the value of $\Delta E^{o}_{v\to s,P}$ for a given solute (vide supra). But the mole fraction of P (in S) in equilibrium with P vapor at the vapor pressure of pure liquid P may be calculated from the equation.

$$X_P^{(s)} = \frac{P_P^o \bar{V}_s}{RT} \exp\left(-\Delta G^{o}_{v\to s,P}/RT\right) \tag{55}$$

provided P_P^o (the vapor pressure of pure liquid P) is known. Since the activity of P is unity under these conditions, the limiting activity coefficient of P in S can be calculated from

$$\gamma_P^{\infty} = \frac{1}{X_P^{(s)}} = \frac{RT}{P_P^o \bar{V}_s} \exp\left(\Delta G^{o}_{v\to s,P}/RT\right) \tag{56}$$

By using the calculated value $\Delta G^{o}_{v\to s,H_2O}$ = -1890 cal for water dissolved in diphenylmethane (see Table 3) and the known vapor pressure of H_2O at 25° (23.7 Torr) one may calculate the value $\gamma^{\infty}_{H_2O}$ = 192, whereas the

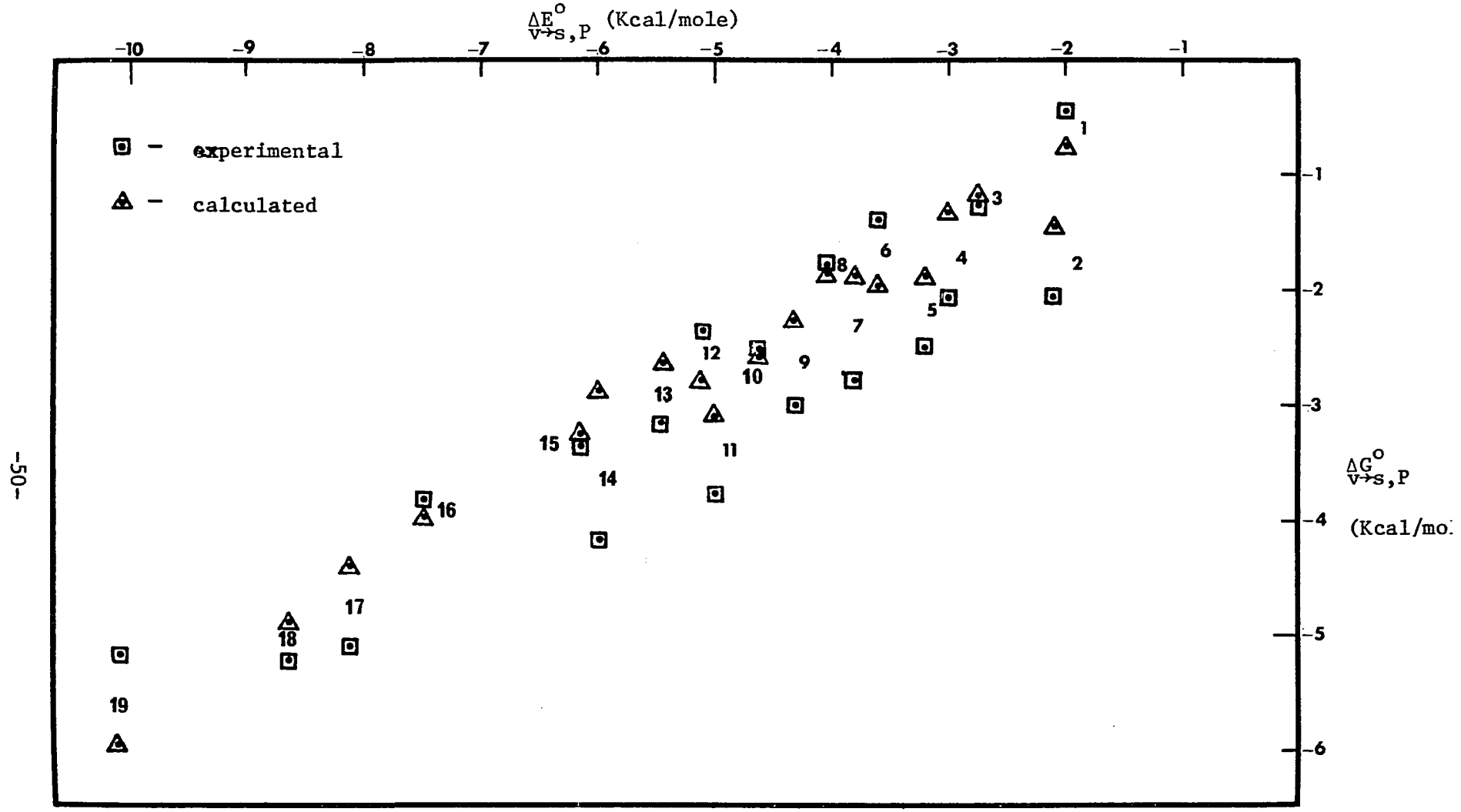


Figure 11: Correlation of energy and free energy of transfer of polar solutes into infinitely dilute solution in nonpolar solvents at 25°C.

LEGEND FOR FIGURE 11

1, water (W) in hexadecane (HXD); 2, trifluoroacetic acid (TFA) in cyclohexane (CHX); 3, methanol (M) in HXD; 4, $(TFA)_2$ in CHX; 5, TFA in CCl_4; 6, SO_2 in heptane (HPT); 7, $(TFA)_2$ in CCl_4; 8, W in diphenylmethane (DPM); 9, $(TFA)_2$ in C_6H_6; 10, trimethylamine (TMA) in HPT; 11, TFA in C_6H_6; 12, M in DPM; 13, diethylamine (DEA) in HXD; 14, M·DEA in HXD; 15, DEA in DPM; 16, W·DEA in HXD; 17, M·DEA in DPM; 18, W·DEA in DPM; 19, TMA·SO_2 in HPT.

Standard states of solutes are 1 molar, ideal dilute solution for vapor and condensed phases.

experimental value is $\gamma^{\infty}_{H_2O} = 227$.

Other, more elaborate theories of nonpolar binary mixtures (such as the recent theory of Flory,[66-68] which employs a reduced partition function, formulated in terms of segment volumes and segment interaction energies) may be utilized to calculate ΔE^{o}_{dil} and ΔG^{o}_{dil} in terms of molecular parameters of the solvent and the nonpolar analog of P. However, since the difference between ΔE^{o}_{dil} and ΔG^{o}_{dil} obtained from various statistical theories are small compared with uncertainties in these quantities for most polar solutes, the relations which can be derived for utilizing these theories with the NPA model are not pursued further here.

CHAPTER IV

APPLICATION OF THE NONPOLAR ANALOG MODEL FOR PREDICTION OF THE EFFECTS OF SOLVENTS ON FREE ENERGIES OF FORMATION OF MOLECULAR COMPLEXES[152]

Applications of the nonpolar analog model method for calculating $\Delta G^{o}_{v\to s,i}$ from $\Delta E^{o}_{v\to s,i}$ for component i which participates in complex formation reactions should be useful in predicting media effects on the complex formation constants, or on free energies of formation of molecular complexes. By substituting with the relation

$$K_{D,i} = \exp\ (-\Delta G^{o}_{v\to s,i}/RT) \tag{57}$$

the equation 16 may be rearranged to give

$$\frac{K_c^{(v)}}{K_c^{(s)}} = \exp\ [(\Delta G^{o}_{v\to s,DA} - \Delta G^{o}_{v\to s,D} - \Delta G^{o}_{v\to s,A})/RT] \tag{58}$$

Thus the ratio of complex formation constants in the gas phase and the solvent phase may therefore be predicted by calculating $\Delta G^{o}_{v\to s,i}$ with employment of the nonpolar analog model. By applying the same reaction to another solvent system the ratio of complex formation constants in two different media may be predicted.

The results of application of the nonpolar analog model method to actual electron donor-acceptor complex formation reactions are given in Table 4. The predicted values of changes in ΔG^{o} for complex formation reactions generally agree with experimental values to within a few hundred calories, although for methanol·diethylamine formation reaction in diphenylmethane, the discrepancy is about 1 Kcal. The agreement is probably satisfactory, considering the fact that several experimental $\Delta E^{o}_{v \to s,i}$ values, each of which is uncertain by several tenths of a kilocalorie, are involved in calculating a single $\Delta G^{o}(s)$ value. As was discussed in chapter II, when the quasi-lattice model method is employed for calculation of $\Delta E^{o}_{v \to s,i}$ for the complex DA, no energy of stabilization is introduced to account for the interaction between the excess dipole moment of the complex and the solvent. One would, therefore, expect the lattice model to lead to values of $\Delta G^{o}(s)$ smaller than experimental values because of the complex dipole-solvent interaction; the effect is apparently most important in the case of methanol.diethylamine in diphenylmethane, where the calculated $-\Delta G^{o}(s)$ is about 1 Kcal less than the observed value. It is known that complexes of aliphatic amines with water and alcohols possess dipole moments which are significantly greater than the vextor sum of the dipole moments of the monomers. Also, the possibility exists that retardation effects are not insignificant in systems where highly polar molecules, with exposed n-electron pairs, interact with an araomatic solvent.[41,42]

TABLE 4

EFFECTS OF MEDIA ON MOLECULAR COMPLEX FORMATION EQUILIBRIA: COMPARISON OF EXPERIMENTAL AND CALCULATED GIBBS FREE ENERGY VALUES FOR FORMATION OF COMPLEXES FROM MONOMERS. t=25°C

Complex	Medium[a]	$-\Delta G^{o}$ (calcd.)[b] (Kcal/mole)	$-\Delta G^{o}$ (calcd.)[c] (Kcal/mole)	$-\Delta G^{o}$ (exptl.) (Kcal/mole)
Diethylamine·H_2O	vapor			1.22[33]
Diethylamine·H_2O	HXD	1.77	1.18	1.41[33]
Diethylamine·H_2O	DPM	0.94	0.39	1.27[33]
$CH_3OH \cdot H_2O$	vapor			1.54[33]
$CH_3OH \cdot H_2O$	HXD	0.61	1.26	1.28[33]
$CH_3OH \cdot H_2O$	DPM	-0.12	0.03	0.92[33]
Trimethylamine·SO_2	vapor			3.40[30]
Trimethylamine·SO_2	HPT	4.74		4.58[30]
$(CF_3COOH)_2$	vapor			5.11[31]
$(CF_3COOH)_2$	CHX	3.57		3.12[31]
$(CF_3COOH)_2$	C_6H_6	1.23		0.57[31]
$(CF_3COOH)_2$	CCl_4	3.22		2.96[31]

[a] HXD=hexadecane, DPM=diphenylmethane, HPT=heptane, CHX=cyclohexane;

[b] Calculated from the lattice model of Stevens, et al;

[c] Calculated from experimental $\Delta E^{o}_{v \to s,P}$, using the NPA method and solubility parameter theory.

CHAPTER V

THERMODYNAMIC PROPERTIES OF DILUTE SOLUTION --- ORIENTATION EFFECTS IN DILUTE AQUEOUS SOLUTION

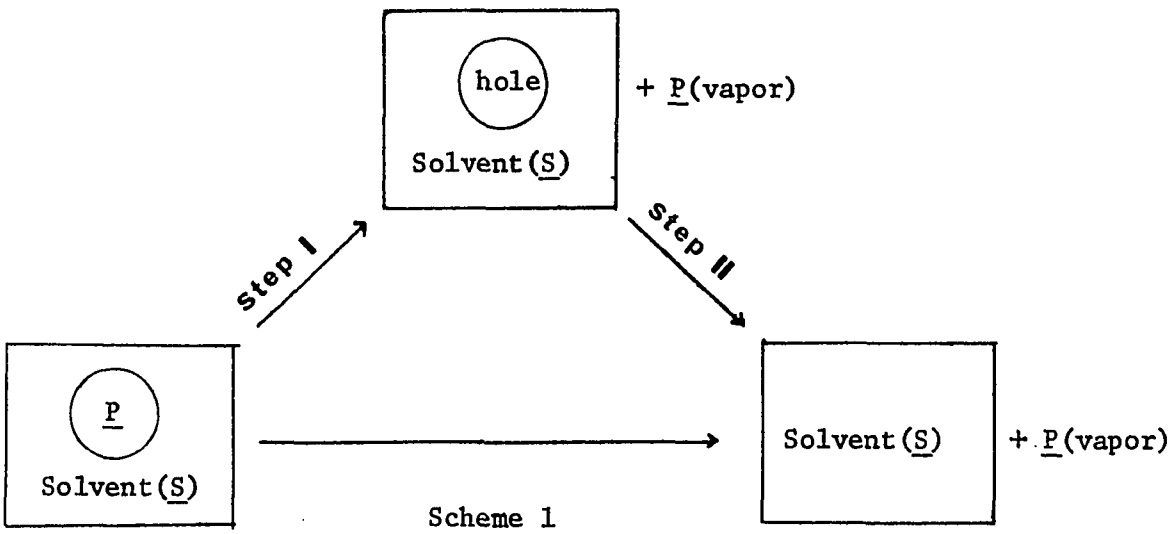
Nonaqueous Solutions

The simple lattice model of dilute binary solutions by Stevens, et al.,[31,32,40] where the solute and the solvent molecules interact via specific interaction sites, was reasonably successful in calculating the internal energy of vaporization of a solute from the liquid solvent by utilizing a certain number of interaction sites and their respective empirical interaction energy parameters. Earlier, Langmuir[69] had used the surface energy of the groups, the group contact areas, and empirical mixture energy to calculate the energy of transfer of a solute from the liquid phase to the vapor in the binary solution. In his treatment any particular group in a large organic molecule was assumed to be characteristic of that group, independent of the nature of the rest of the molecule.

Consider the following model for vaporizing a solute: The solute molecule (P) may be considered to exist within a cavity in the solvent (S), and solute molecules (P) are in contact only with the solvent molecules which surround them. The solute molecule located inside the cavity and the adjacent solvent molecules are assumed to

interact with each other uniformly along the surface of the cavity; specific interaction sites with different energies are not assumed to exist as in the lattice model.

The volume of the cavity is taken to be equal to the molar volume of the pure solute, and the solute molecules are assumed to be spherical. The molar energy of vaporiation of the solute from the infinitely dilute solution, $-\Delta E^{o}_{v\to s,P}$, may be calculated by using the cycle illustrated in Scheme 1.



Scheme 1

In step I, the solute molecule, which is surrounded by the solvent molecules, is removed from the solvent phase to become vaporized, leaving a hole (empty cavity) behind in the bulk solvent. In step II, the hole collapses, leaving the pure liquid solvent.

The molar energy change accompanying step I may be written as

$$\Delta E^{o}_{I} = \eta A_{P}\, \xi_{ps} \tag{59}$$

where η is Avogadro's number, A_p is the molecular surface area of the spherical cavity occupied by the solute molecule, and ξ_{ps} is the average interfacial energy per unit surface area between the solute and the solvent molecules.

The molar energy change accompanying step II may be written as

$$\Delta E^o_{II} = -\frac{1}{2}\eta A_p \xi_{ss} \tag{60}$$

where ξ_{ss} is the interfacial energy per unit surface area between two solvent molecules. The factor 1/2 accounts for the fact that when the surface collapses the interfacial area formed is one half of the original cavity surface area, because it takes two opposing surfaces to make an interface.

ξ_{ss} may be related to the molar energy of vaporization of the pure liquid solvent (S), $\Delta E_S^{o\,vap}$, by

$$\Delta E_S^{o\,vap} = \frac{1}{2}\eta A_s \xi_{ss} \tag{61}$$

where A_s is the molecular surface area of the solvent molecule.

Likewise, ξ_{pp}, the interfacial energy per unit area between two solute molecules, may be related to the molar energy of vaporization of the pure liquid solute (P), $\Delta E_P^{o\,vap}$, by

$$\Delta E_P^{o\,vap} = \frac{1}{2}\eta A_p \xi_{pp} \tag{62}$$

Therefore, the molar energy of vaporization of the solute P from the liquid solvent S, $-\Delta E^o_{v\to s,P}$, may be expressed as

$$-\Delta E^{o}_{v\to s,P} = \Delta E^{o}_{I} + \Delta E^{o}_{II}$$

$$= \eta A_p \left(\xi_{ps} - \frac{1}{2}\xi_{ss}\right) \qquad (63)$$

To evaluate[a] ξ_{ps}, one may use observed values of $\Delta E^{o}_{v\to p,S}$, the molar energy of vaporization of molecules S (taken as solute) from dilute solution in P (taken as solvent). Based upon the cycle of Scheme 1, $-\Delta E^{o}_{v\to p,S}$ may be expressed as

$$-\Delta E^{o}_{v\to p,S} = \eta A_s \left(\xi_{ps} - \frac{1}{2}\xi_{pp}\right) \qquad (64)$$

by analogy with equation 63.

Solving equation 64 with respect to ξ_{ps} and use of ξ_{pp} from equation 62 leads to the relation

$$\xi_{ps} = \frac{-\Delta E^{o}_{v\to p,S}}{\eta A_s} + \frac{\Delta E^{o\,vap}_{P}}{\eta A_p} \qquad (65)$$

Substitution of equation 65 into equation 63 along with equation 61 yields

$$-\Delta E^{o}_{v\to s,P} = \Delta E^{o\,vap}_{P} - \frac{\bar{A}_p}{\bar{A}_s}\left(\Delta E^{o}_{v\to p,s} + \Delta E^{o\,vap}_{S}\right) \qquad (66)$$

where $\bar{A}_p$ and $\bar{A}_s$ are the molar surface area of the solute and the solvent, respectively.

The corresponding free energy relation, obtained similarly, will then be

$$-\Delta G^{o}_{v\to s,P} = \Delta G^{o\,vap}_{P} - \frac{\bar{A}_P}{\bar{A}_S}\left(\Delta G^{o}_{v\to p,S} + \Delta G^{o\,vap}_{S}\right) \qquad (67)$$

where ΔG^{o} denotes the standard molar free energy change with the standard states of unit molarity of the ideal solution in the liquid phase and unit molarity of the ideal gas in the vapor phase, respectively.

Equation 66 will enable us to predict the energy of vaporization of a solute (P) in the dilute solution where S is the solvent from the corresponding energy from the system of S as the solute in the dilute solution with P as the solvent. Based upon the limited number of published experimental data available, calculated values of $-\Delta E^{o}_{v\to s,P}$ from equation 66 and of $-\Delta G^{o}_{v\to s,P}$ from equation 67 are tabulated along with experimental values in Tables 5 and 6. Calculated and experimental results are in good general agreement, considering the uncertainties involved in the experimental values and the assumptions made that all the species are spherical in shape. Deviations which occurs in the systems, such as a polar solute in a nonpolar solvent and vice versa or a polar solute in a polar solvent is attributed to failure of the assumption that interaction energy per unit area between a single P molecule and the bulk S, ξ_{ps}, is same as that between a single S molecule and the bulk P, ξ_{sp}. Complications are caused by polar and particularly hydrogen bonded molecules. The proposed model ignores the orientation effect which comes into existence when nonpolar solutes dissolve in polar solvents, although there is no ordering effect to be considered in the system where polar solutes are surrounded by nonpolar solvents.

For convenience this model will be referred to as the Interfacial Energy model.

TABLE 5

CALCULATED VALUES OF ENERGY OF SOLUTION FROM VAPOR PHASE.

$t=25^{\circ}C$ UNLESS OTHERWISE NOTED

System (P + S)	$\Delta E_P^{\circ\infty}$ dilution (cal/mole)	$-\Delta E^{\circ}_{v\to s,P}$ (calcd.) (cal/mole)	$-\Delta E^{\circ}_{v\to s,P}$ (exptl.) (cal/mole)
$C_6H_{14} + CCl_4$	180	6728	6770[83]
$CCl_4 + C_6H_{14}$	290	7004	6950[83]
$C_6H_{12} + CCl_4$	144	7164	7176[84]
$CCl_4 + C_6H_{12}$	140	7110	7226[85]
$C_6H_6 + CCl_4$	113	7394	7397[86]
$CCl_4 + C_6H_6$	123	7120	7117[86]
$C_6H_6 + C_6H_{12}$	745	6776	6765[86]
$C_6H_{12} + C_6H_{12}$	840	6466	6480[86]
$C_6H_6 + C_7H_{16}$	741	6636	6769[87]
$C_7H_{16} + C_6H_6$	1227	7108	6923[87]
$C_6H_6 + c\text{-}C_6H_{11}C_2H_5$	1044	7063	6466[88]
$c\text{-}C_6H_{11}C_2H_5 + C_6H_6$	612	7648	8460[88]
$C_6H_6 + o\text{-}C_6H_4(CH_3)_2$	232	7353	7278[89]
$o\text{-}C_6H_4(CH_3)_2 + C_6H_6$	193	9473	9596[89]
$C_6H_6 + m\text{-}C_6H_4(CH_3)_2$	253	7353	7257[89]
$m\text{-}C_6H_4(CH_3)_2 + C_6H_6$	195	9293	9414[89]
$C_6H_6 + p\text{-}C_6H_4(CH_3)_2$	196	7400	7314[89]
$(CH_3)_2CO + C_2H_5CN$	-80	7152	7154[93]

TABLE 5 continued

System (P + S)	$\Delta E_P^{o\,\infty}$ dilution (cal/mole)	$-\Delta E^o_{v\to s,P}$ (calcd.) (cal/mole)	$-\Delta E^o_{v\to s,P}$ (exptl.) (cal/mole)
$C_2H_5CN + (CH_3)_2CO$	-80	8400	8398[93]
$i\text{-}C_3H_7OH + (CH_3)_2CHNH_2$	-1950	15003	14696[93]
$(CH_3)_2CHNH_2 + i\text{-}C_3H_7OH$	-2438	8112	8444[93]
$i\text{-}C_3H_7OH + C_2H_5CN$	513	12203	12233[93]
$C_2H_5CN + i\text{-}C_3H_7OH$	513	7832	7805[93]
$(CH_3)_2CHNH_2 + C_2H_5CN$	197	5667	5809[93]
$C_2H_5CN + (CH_3)_2CHNH_2$	297	8145	8021[93]
$C_2H_5OH + CH_3CN$	1930	7990	7690[93]
$CH_3CN + C_2H_5OH$	1513	5972	6252[93]
$(C_2H_5)_2O + c\text{-}C_6H_{12}$	420	5508	5496[94]
$c\text{-}C_6H_{12} + (C_2H_5)_2O$	420	6969	6882[94]
$C_5H_5N + c\text{-}C_6H_{11}C_2H_5$	1570	7896	7490[88]
$c\text{-}C_6H_{11}C_2H_5 + C_5H_5N$	1702	6782	7378[88]
$c\text{-}C_6H_{11}C_2H_5 + \alpha\text{-}C_5H_4(CH_3)N$	200	8868	8860[88]
$C_5H_5N + C_6H_5C_2H_5$	200	8868	8860[88]
$C_6H_5C_2H_5 + C_5H_5N$	254	9234	9246[88]
$p\text{-}C_6H_4(CH_3)_2 + C_6H_6$	137	9290	9398[89]
$C_6H_6 + C_6H_5CH_3$	223	7301	7387[90]
$C_6H_5CH_3 + C_6H_6$	236	8237	8254[90]
$c\text{-}C_6H_{12} + C_6H_5CH_3(20^oC)$	657	6747	6753[104]
$C_6H_5CH_3 + c\text{-}C_6H_{12}(20^oC)$	472	8022	8018[104]

TABLE 5 continued

System (P + S)	$\Delta E_P^{o,\infty}$ dilution (cal/mole)	$-\Delta E^o_{v\to s,P}$ (calcd.) (cal/mole)	$-\Delta E^o_{v\to s,P}$ (exptl.) (cal/mole)
$C_6H_5C_2H_5$ + c-$C_6H_{11}CH_3$	420	9090	9080[88]
c-$C_6H_{11}CH_3$ + $C_6H_5C_2H_5$	421	7429	7439[88]
$C_6H_5CH_3$ + c-$C_6H_{11}C_2H_5$	527	9064	8973[88]
c-$C_6H_{11}C_2H_5$ + $C_6H_5CH_3$	481	8499	8599[88]
C_6H_{14} + c-C_6H_{12}	298	6765	6652[91]
c-C_6H_{12} + C_6H_{14}	162	7058	7158[91]
c-C_7H_{16} + C_6H_{12}(20^oC)	252	7840	7899[104]
c-C_6H_{12} + C_7H_{16}(20^oC)	123	7219	7197[104]
C_6H_5F + c-C_6H_{12}(30^oC)	230	7921	7900[92]
c-C_6H_{12} + C_6H_5F(30^oC)	220	7077	7100[92]
$(CH_3)_2CO$ + i-C_3H_7OH	2065	5343	5009[93]
i-C_3H_7OH + $(CH_3)_2CO$	1777	10625	10969[93]
$(CH_3)_2CO$ + $(CH_3)_2CHNH_2$	-951	5900	8025[93]
$(CH_3)_2CHNH_2$ + $(CH_3)_2CO$	1303	7060	4703[93]
$C_6H_5C_2H_5$ + α-$C_5H_4(CH_3)N$	67	9458	9433[88]
C_6H_5F + C_6H_6	-463	8309	8593[95]
C_6H_6 + C_6H_5F	-173	7955	7683[95]
CH_3OH + C_6H_6	1585	8394	6974[96]
C_6H_6 + CH_3OH	277	4842	7233[96]
C_6H_6 + C_2H_5OH	506	4360	7004[126]
C_2H_5OH + C_6H_6	2391	9251	7244[126]

TABLE 5 continued

System (P + S)	$\Delta E_P^{o\infty}$ dilution (cal/mole)	$-\Delta E^o_{v\to s,P}$ (calcd.) (cal/mole)	$-\Delta E^o_{v\to s,P}$ (exptl.) (cal/mole)
$c\text{-}C_6H_{12}$ + C_2H_5OH	949	4730	6371[126]
C_2H_5OH + $c\text{-}C_6H_{12}$	1717	9006	7919[126]
$n\text{-}C_6H_{14}$ + $o\text{-}C_6H_4(CH_3)_2$	400	6492	6580[122]
$o\text{-}C_6H_4(CH_3)_2$ + $n\text{-}C_6H_{14}$	460	9413	9330[122]
C_5H_5N + CCl_4	-10	8733	9070[127]
CCl_4 + C_5H_5N	370	7251	6870[127]
CCl_4 + $C_6H_5CH_3$	350	7254	7190[127]
$C_6H_5CH_3$ + CCl_4	-15	8436	8505[127]

TABLE 6

CALCULATED VALUES OF FREE ENERGY OF SOLUTION FROM THE VAPOR PHASE[†]

t=25°C UNLESS OTHERWISE INDICATED

System (P + S)	γ_P^∞	$-\Delta G^o_{v\to s,P}$ (calcd.) (cal/mole)	$-\Delta G^o_{v\to s,P}$ (exptl.) (cal/mole)
$CH_3OH + CCl_4$	15.874	1930	3200[106]
$CCl_4 + CH_3OH$	7.498	1451	3715[106]
$C_6H_5Cl + C_6H_6$	1.029	5501	5758[107]
$C_6H_6 + C_6H_5Cl$	1.088	4906	4422[107]
$CCl_4 + C_2Cl_4$(70°C)	1.004	4006	3934[108]
$C_2Cl_4 + CCl_4$(70°C)	1.005	4905	4970[108]
$c\text{-}C_5H_{10} + CCl_4$	1.057	3795	3809[109]
$CCl_4 + c\text{-}C_5H_{10}$	1.057	4394	4379[109]
$n\text{-}C_6H_{14} + C_6H_6$	2.065	3321	3850[110]
$C_6H_6 + n\text{-}C_6H_{14}$	1.723	4404	3999[110]
$CCl_4 + C_6H_5CH_3$(35°C)	1.032	4173	4072[111]
$C_6H_5CH_3 + CCl_4$(35°C)	1.033	4803	4906[111]
$2,2,4\text{-}C_5H_9(CH_3)_3 + CCl_4$(40°C)	1.331	3901	4362[112]
$CCl_4 + 2,2,4\text{-}C_5H_9(CH_3)_3$(40°C)	1.166	4246	3913[112]
$C_6H_6 + m\text{-}C_6H_4(CH_3)_2$	1.047	4686	4334[113]
$m\text{-}C_6H_4(CH_3)_2 + C_6H_6$	1.047	5533	5972[113]
$CS_2 + CCl_4$	1.219	4200	3597[114]
$CCl_4 + CS_2$	1.445	3610	4447[114]
$C_6H_6 + C_2H_5OH$	1.583	2366	4528[115]

TABLE 6 continued

System (P + S)	γ_P^∞	$-\Delta G^o_{v\to s,P}$ (calcd.) (cal/mole)	$-\Delta G^o_{v\to s,P}$ (exptl.) (cal/mole)
$C_2H_5OH + C_8H_6$	16.608	5063	3422[115]
$c\text{-}C_5H_{10} + C_2Cl_4$	1.346	3684	3581[116]
$C_2Cl_4 + c\text{-}C_5H_{10}$	1.346	5207	5315[116]
$n\text{-}C_5H_{12} + C_6H_6$	2.059	2735	3130[117]
$C_6H_6 + n\text{-}C_5H_{12}$	1.938	4331	4005[117]
$c\text{-}C_5H_{10} + C_6H_6$	1.548	3444	2944[117]
$C_6H_6 + c\text{-}C_5H_{10}$	1.671	3734	4212[117]
$c\text{-}C_6H_{12} + C_6H_6$	1.855	3957	4174[117]
$C_6H_6 + c\text{-}C_6H_{12}$	1.616	4340	4151[117]
$n\text{-}C_7H_{16} + C_6H_6$	2.228	3894	4513[117]
$C_6H_6 + n\text{-}C_7H_{16}$	1.557	3432	3991[117]
$3\text{-}C_6H_{13}(CH_3) + C_6H_6$	2.117	3667	4352[117]
$C_6H_6 + 3\text{-}C_6H_{13}(CH_3)$	1.675	4440	3953[117]
$2,4\text{-}C_5H_{10}(CH_3)_2 + C_6H_6$	2.790	3491	3927[117]
$C_6H_6 + 2,4\text{-}C_5H_{10}(CH_3)_2$	2.006	4346	3834[117]
$2,2,3\text{-}C_4H_7(CH_3)_3 + C_6H_6$	2.250	3392	4031[117]
$C_6H_6 + 2,2,3\text{-}C_4H_7(CH_3)_3$	1.651	4375	3964[117]
$c\text{-}C_6H_{11}(CH_3) + C_6H_6$	1.681	4112	4673[117]
$C_6H_6 + c\text{-}C_6H_{11}(CH_3)$	1.654	4482	4042[117]
$n\text{-}C_6H_{14} + C_6H_5CH_3$	1.773	3613	3831[117]
$C_6H_5CH_3 + n\text{-}C_6H_{14}$	1.678	4948	4730[117]

TABLE 6 continued

System (P + S)	γ_P^∞	$-\Delta G^o_{v\to s,P}$ (calcd.) (cal/mole)	$-\Delta G^o_{v\to s,P}$ (exptl.) (cal/mole)
$3\text{-}C_5H_{11}(CH_3) + C_6H_5CH_3$	1.668	3369	3734[117]
$C_6H_5CH_3 + 3\text{-}C_5H_{11}(CH_3)$	1.834	5003	4683[117]
$c\text{-}C_6H_{12} + C_6H_5CH_3$	1.590	4094	4156[117]
$C_6H_5CH_3 + c\text{-}C_6H_{12}$	1.687	4902	4840[117]
$c\text{-}C_5H_9(CH_3) + C_6H_5CH_3$	1.511	3881	3983[117]
$C_6H_5CH_3 + c\text{-}C_5H_9(CH_3)$	1.576	4957	4859[117]
$C_7H_{16} + C_6H_5CH_3$	1.608	4274	4596[117]
$C_6H_5CH_3 + C_7H_{16}$	1.264	5090	4830[117]
$c\text{-}C_6H_{11}(CH_3) + C_6H_5CH_3$	1.344	4392	4697[117]
$C_6H_5CH_3 + c\text{-}C_6H_{11}(CH_3)$	1.461	5101	4830[117]
$2,2,4\text{-}C_5H_9(CH_3)_3 + C_6H_5CH_3$	1.885	3799	4461[117]
$C_6H_5CH_3 + 2,2,4\text{-}C_5H_9(CH_3)_3$	1.710	5077	4583[117]
$2\text{-}C_5H_{11}(CH_3) + C_6H_6$	2.574	2982	3521[117]
$C_6H_6 + 2\text{-}C_5C_{11}(CH_3)$	1.946	4319	3923[117]
$2,2\text{-}C_4H_8(CH_3)_2 + C_6H_6$	2.698	2742	3251[117]
$C_6H_6 + 2,2\text{-}C_4H_8(CH_3)_2$	1.992	4293	3906[117]
$c\text{-}C_5H_9(CH_3) + C_6H_6$	1.706	4405	4020[117]
$C_6H_6 + c\text{-}C_5H_9(CH_3)$	1.729	3568	4089[117]
$n\text{-}C_8H_{18} + C_6H_6$	1.946	4533	5289[117]
$C_6H_6 + n\text{-}C_8H_{18}$	1.683	4314	3885[117]
$2,2,4\text{-}C_5H_9(CH_3)_3 + C_6H_6$	2.416	3529	4421[117]

TABLE 6 continued

System (P + S)	γ_P^∞	$-\Delta G^\circ_{v\to s,P}$ (calcd.) (cal/mole)	$-\Delta G^\circ_{v\to s,P}$ (exptl.) (cal/mole)
C_6H_6 + 2,2,4-$C_5H_9(CH_3)_3$	1.709	4450	3868[117]
C_6H_6 + CH_3OH	7.87	1040	3796[123]
CH_3OH + C_6H_6	15.3	4394	2769[123]
c-C_6H_{12} + CH_3OH	10.17	316	3448[124]
CH_3OH + c-C_6H_{12}	11.70	4153	250[124]
$CHCl_3$ + CCl_4	1.188	4028	3971[125]
CCl_4 + $CHCl_3$	1.188	4455	4395[125]

† Standard states are unit molarity, ideal dilute solution for vapor and liquid phases.

Aqueous Solutions

Aqueous solutions have long been considered to be peculiar themodynamically.[37,38,78] The peculiarities, such as excessively negative entropy changes for the transfer of solutes from the vapor phase into water, very low solubility of the nonpolar or the slightly polar solutes and the abnormally high partial molar heat capacities of solutes in the aqueous solutions, have seemed to many investigators to be related to the peculiar thermodynamic properties of the pure liquid water. Indeed, liquid water exhibits numerous properties very different from those of ordinary organic solvents and hydride compounds of the other members of the oxygen family. Water has a maximum density at $4^{\circ}C$, and large values of the dielectric constant, heat capacity, viscosity, melting point, boiling point, heat of fusion, heat of vaporization, thermal conductivity, and critical temperature. These unique properties have been attributed to the structuredness of the pure liquid water and the existense of extensive hydrogen-bonded networks.

1. The Structure of Liquid Water

The first major work reported on the structure of liquid water is the one by Bernal and Fowler[70] in 1933. By considering X-ray diffraction results, they proposed a model in which water molecules are held together in different ways at three different temperature regions. Below $200^{\circ}C$ the intermolecular arrangements were postulated as four-coordinated tetrahedral ones but with slight difference at

temperatures above and below $4^{o}C$.

In the interstitial model,[71] non-hydrogen-bonded monomeric water molecules occupy the cavities enclosed by the lattices; the clathrate model[72] assumes that aqueous systems are quasi-crystalline, and that monomeric water molecules are located as guest molecules, which are not hydrogen-bonded, in cages consisting of many water molecules per unit.

Frank[73,74] postulated that liquid water consists of a continuous distribution of three-dimensionally hydrogen-bonded clusters of the clathrate structures of various size consistently flickering "on" and "off". The life-time of clusters is short as is shown by the dielectric relaxation time on the order of 10^{-11} sec., but still long in comparison with the molecular vibration time which is 100 to 1000 times shorter.

Based upon the Frank's model of mixtures of clusters, Hagler, et al.,[75] applied a modified significatn structure theory to their statistical treatment for 0, 1, 2, 3, or 4 coordinated clusters of all possible sizes. Their calculation indicated that the size of most clusters is not more than 60 or 70 molecules and that the median cluster size of the distribution is about 11 at $0^{o}C$ and decreases with increasing temperature. This model accounts for many of the properties of water, such as the maximum in the density and the decrease in the intensity of intermolecular vibration as temperature increases.

The significant structure theory was applied by Jhon, et al.,[76] to the model of liquid water in which two species of solid-like water molecules are in equilibrium, that is, cage-like clusters of ice-I-like structure and a denser ice-III-like structure. This model postulates

that most of the ice-I-like structure deforms into a denser ice-III-like structure upon melting, and the volume decrease continues until the temperature reaches 4°C, at which point most of the ice-I-like structure has been destroyed. Above 4°C, water begins to behave as a normal liquid.

In contrast to these mixture models of the water structure, a continuous model of water structure was proposed by Pople.[77] In this model water molecules experience distortion of hydrogen bonds, which are bent but not broken, as the temperature rises. At the melting point of ice a breakdown of the long-range order occurs. After fusion the four hydrogen bonds from one molecule of water are regarded to be able to bend independently because of the resulting rupture of the long-range order of the lattice.

Thus, although distinct schools of thought continue to exist, at present there seems to be no generally accepted model for the structure of liquid water.

2. Orientation Effects

Earlier,[37,78] abnormally negative values of the entropy of solution in the aqueous media were attributed to formation of a cavity, which results in a loss of degrees of freedom of the total system, solute plus solvent. Following the proposal of the concept of iceberg formation,[38] in which the water molecules are assumed to build a microscopic "iceberg" around each solute molecule, much research has been done in an attempt to elucidate the peculiar structure of dilute aqueous solutions. In particular, the hydrophobic bonding concept[79,80] has been

advanced to explain biochemical processes in terms of the presumed increased order of water molecules surrounding the nonpolar groups of solutes. In order to understand the origin and the reality of the hydrophobic bond, the problem of molecular interactions involved in aqueous solutions must first be solved.

Herman[81] applied the significant structure theory of the liquid to aqueous solutions by using a model in which water molecules surrounding the solute molecules have increased order and the first layer water molecules are in an asymmetric electric field which does not exist in the pure bulk water. However, values of the heat capacity calculated in this way are too low.

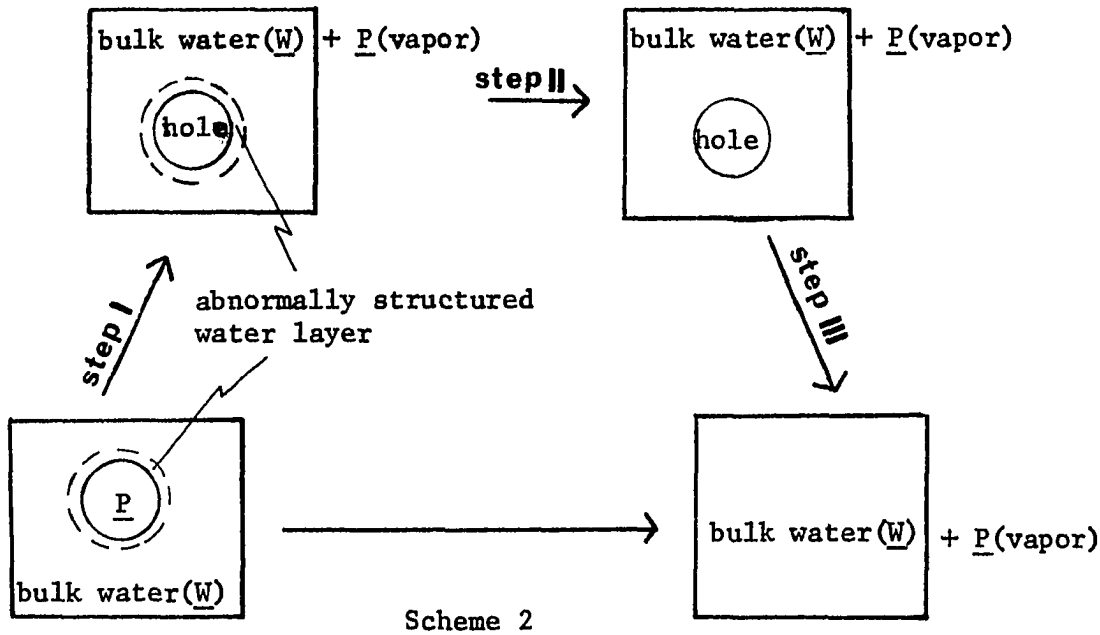
Nemethy and Scheraga,[82] employing the concept of the iceberg formation, concluded that solute molecules are surrounded by 4-hydrogen-bonded water clusters, which are energetically most favorable of the five distributed energy levels.

Theories thus far proposed for the abnormal behavior of aqueous solutions do not agree well with experimental observations and each statistical theory has involved doubtful assumptions inevitable in formulating and calculating partition functions.

As a way to avoid difficulties arising from formulating the partition functions, let us now consider a more classical model of aqueous solutions in which all the factors causing abnormality, whatever their origin and significance, are conveniently combined in the term "orientation energy" that arises because of the formation of an abnormally structured layer of water molecules around the foreign solute.

The thermodynamic model proposed here for considering the

vaporization of a solute from the dilute aqueous solution may be separated into three steps illustrated in Scheme 2 below:



Scheme 2

Vaporization is imagined to occur in such a way that the solute molecule, P, which is surrounded by the water molecules with a different structure from that of bulk water, is first torn completely free from its interactions with the water molecules to become vapor, leaving a hole and the abnormally oriented layers of the water molecules (step I). Next, the abnormally ordered water molecules reorient to properties of bulk water (step II), and finally the hole collapses with formation of normal water-water contacts and structure (step III).

By using the Interfacial Energy model which was discussed earlier, all of the changes of energies and free energies occurring in Scheme 2 may be expressed in the same manner as in the nonaqueous solutions except for the thermodynamic changes involved in step II.

Note that steps I and III of Scheme 2 are entirely analogous to steps I and II of Scheme 1 for nonaqueous solutions.

Step II and the energy and free energy changes involved therein are considered to be solely responsible for the abnormal behavior of aqueous solutions. We designate the energy of step II as the orientation energy, $\Delta E^{o}_{orientation}$, and suggest that it ought to be a direct measure of the effect of solvent orientation in dilute aqueous solutions.

The energies involved in steps (I) and (III) will be given by exactly the same relations as those used in the case of the nonaqueous solutions. Hence, the molar energy of solution of a solute P from the vapor phase to pure liquid water, $-\Delta E^{o}_{v\to aq,P}$, may be written as

$$-\Delta E^{o}_{v\to aq,P} = \Delta E^{o}_{I} + \Delta E^{o}_{III} + \Delta E^{o}_{orientation} \tag{68}$$

$$-\Delta E^{o}_{v\to aq,P} = \Delta E_{P}^{o\,vap} - \frac{\bar{A}_P}{\bar{A}_w}\left(\Delta E^{o}_{v\to p,W} + \Delta E_{W}^{o\,vap}\right) + \Delta E^{o}_{orientation} \tag{69}$$

where $\bar{A}_w$, $\Delta E^{o}_{v\to p,W}$ and $\Delta E_{W}^{o\,vap}$ denote the molar surface area of pure liquid water of the spherical shape, the molar energy of solution of water from the vapor phase to liquid P, and the molar energy of vaporization of water, 9912 cal/mole at 25°C, respectively. Here, $\Delta E^{o}_{orientation}$ is the orientation energy for one mole of the solute P dissolved in water. Rearrangement of equation 69 gives

$$-\Delta E^{o}_{orientation} = \Delta E^{o}_{v\to aq,P} + \Delta E_{P}^{o\,vap} - \frac{\bar{A}_P}{\bar{A}_w}\left(\Delta E^{o}_{v\to p,W} + \Delta E_{W}^{o\,vap}\right) \tag{70}$$

By analogy, the corresponding free energy relations are

$$-\Delta G^{o}_{v\rightarrow aq,P} = \Delta G_P^{o\,vap} - \frac{\bar{A}_P}{\bar{A}_w}\left(\Delta G^{o}_{v\rightarrow p,W} + \Delta G_W^{o\,vap}\right) + \Delta G^{o}_{orientation} \qquad (71)$$

$$-\Delta G^{o}_{orientation} = \Delta G^{o}_{v\rightarrow aq,P} + \Delta G_P^{o\,vap} - \frac{\bar{A}_P}{\bar{A}_w}\left(\Delta G^{o}_{v\rightarrow p,W} + \Delta G_W^{o\,vap}\right) \qquad (72)$$

where $\Delta G^{o}_{v\rightarrow aq,P}$, $\Delta G^{o}_{v\rightarrow p,W}$, $\Delta G_W^{o\,vap}$ and $\Delta G^{o}_{orientation}$ denote the molar free energy of solution of P from the vapor phase to pure liquid water, the molar free energy of solution of the water from the vapor phase to liquid P, the molar free energy of vaporization of water, 6326 cal/mole at 25°C, and the molar orientation free energy involved in step II, respectively.

In Figure 12 the calculated $\Delta E^{o}_{orientation}$ and $\Delta G^{o}_{orientation}$ are plotted against the molar surface area of the solutes with both the solute and water molecules treated as being spherical. These plots show that both $\Delta E^{o}_{orientation}$ and $\Delta G^{o}_{orientation}$ are closely correlated with the molar surface arears, and an approximately linear relation is observed.

In Figure 13, $\Delta G^{o}_{orientation}$ and $\Delta E^{o}_{orientation}$ calculated for solutes for which experimental data are available are plotted against each other. These results are empirically well represented by the equation.

$$-\Delta G^{o}_{orientation} = \frac{1}{2}\left(-\Delta E^{o}_{orientation}\right) \qquad (73)$$

Substitution of equation 73 into equation 71 and cancellation of the $\Delta E^{o}_{orientation}$ terms in the resulting equation and in equation 69 lead to

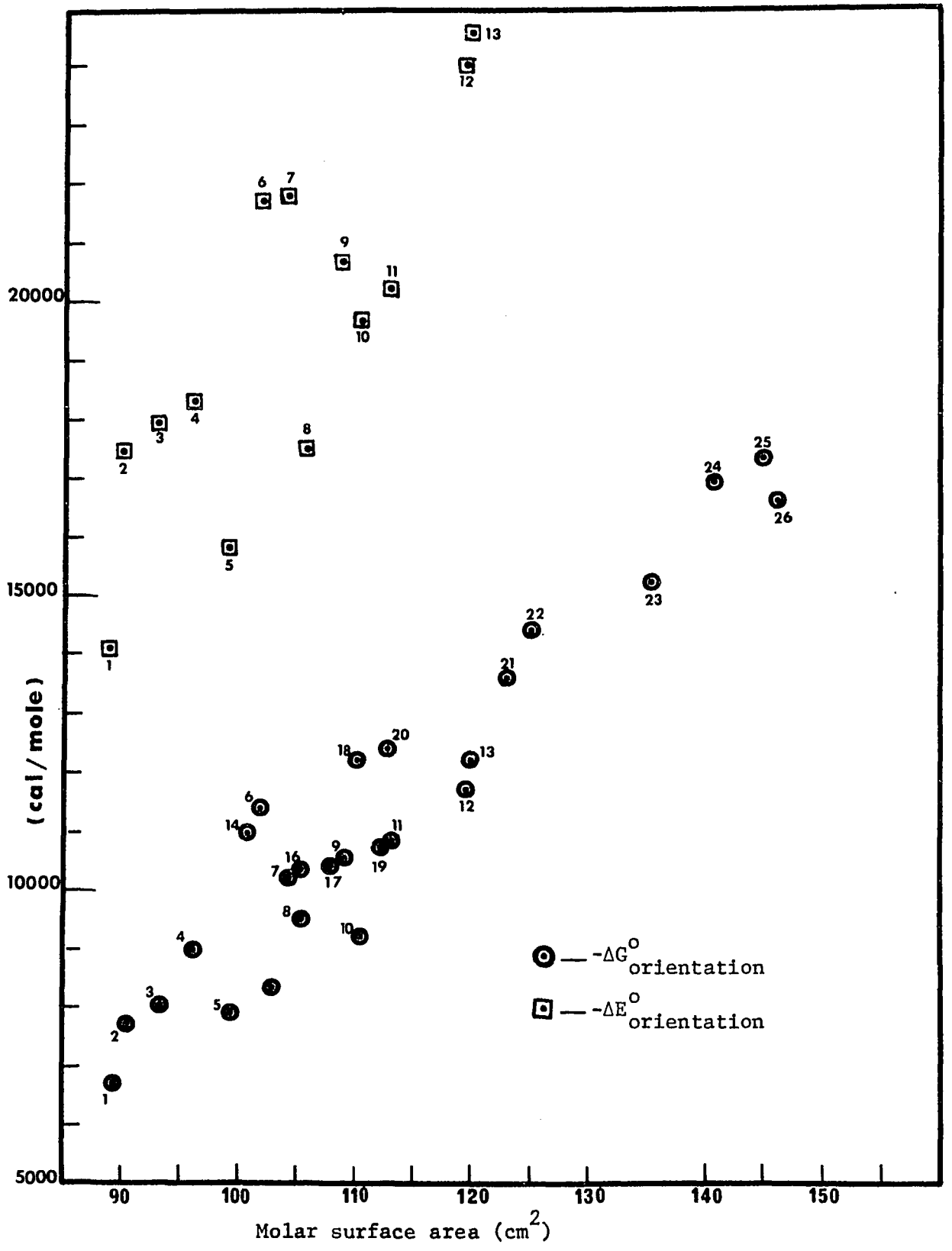


Figure 12: Correl ations of orientation energy and orientation free energy with molar surface area of solutes at 25°C.

LEGEND FOR FIGURE 12

1, CH_2ClCH_2Cl; 2, $CHCl_3$; 3, $CHCl_2CH_3$; 4, C_6H_6; 5, $CHCl_2CH_2Cl$; 6, CCl_4; 7, CCl_3CH_3; 8, C_6H_5Cl; 9, $C_6H_5CH_3$; 10, CCl_3CH_2Cl; 11, o-$C_6H_4Cl_2$; 12, $C_6H_5C_2H_5$; 13, m-$C_6H_4(CH_3)_2$; 14, c-C_5H_{10}; 15, $CH_2ClCHClCH_3$; 16, c-hexene; 17, C_6H_5Br; 18, c-hexane; 19, o-$C_6H_4Cl_2$; 20, c-$C_5H_9CH_3$; 21, c-$C_6H_{11}CH_3$; 22, n-C_6H_{14}; 23, n-C_7H_{16}; 24, $C_6H_5C_4H_9$; 25, n-C_8H_{18}; 26, 2,2,4-$C_5H_9(CH_3)_3$.

Standard states of solutes are 1 molar, ideal dilute solution for vapor and condensed phases.

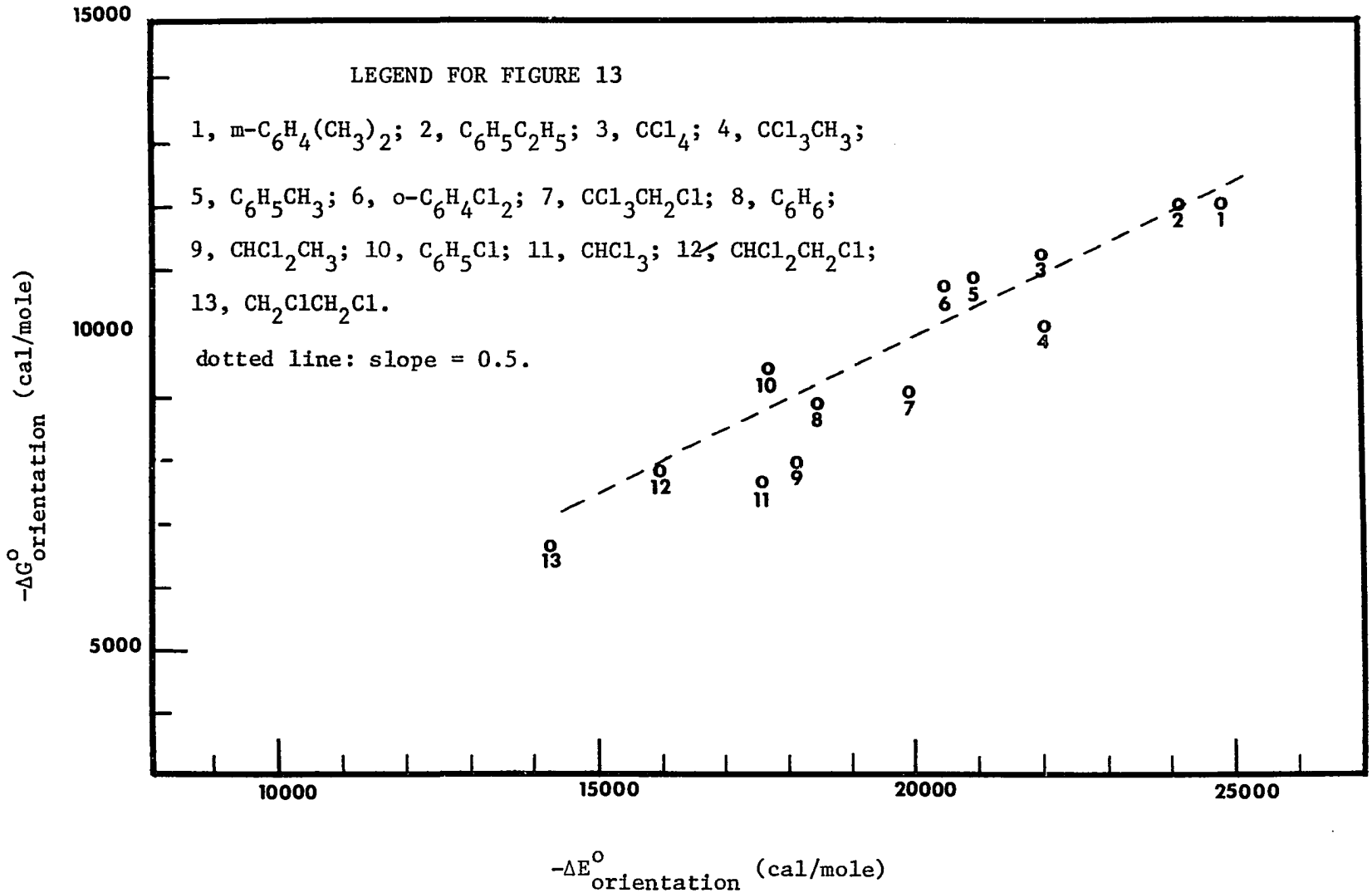


Figure 13: Correlation of orientation energy and orientation free energy at 25°C.

$$[-\Delta E^{o}_{v\rightarrow aq,P} + 2\Delta G^{o}_{v\rightarrow aq,P}] = (\Delta E_P^{o\,vap} - 2\Delta G_P^{o\,vap}) - \frac{\bar{A}_P}{\bar{A}_W}(\Delta E_W^{o\,vap} - 2\Delta G^{o}_{v\rightarrow P,W} +$$

$$\Delta E_W^{o\,vap} - 2\Delta G_W^{o\,vap}) \qquad (74)$$

Now, it is convenient to use the empirical linear relations described previously for expressing $\Delta G^{o}_{v\rightarrow P,W}$ and $-\Delta G_P^{o\,vap}$ as a function of the corresponding energies of transfer. These expressions are

$$\Delta G^{o}_{v\rightarrow P,W} = \beta_P \, \Delta E^{o}_{v\rightarrow P,W} + 300 \quad \text{cal/mole} \qquad (75)$$

$$-\Delta G_P^{o\,vap} = -\beta_P \, \Delta E_P^{o\,vap} + 300 \quad \text{cal/mole} \qquad (76)$$

where β_P is the slope of a plot of $\Delta G^{o}_{v\rightarrow s}$ vs. $\Delta E^{o}_{v\rightarrow s}$ for $\underline{P}$ as the solvent (see Chapter 2). When equations 75 and 76 are substituted into equation 74 one obtains

$$\Delta G^{o}_{v\rightarrow aq,P} = \frac{1}{2}[\Delta E^{o}_{v\rightarrow aq,P} + (1-2\,\beta_P)\,\Delta E_P^{o\,vap} + 600 - \frac{\bar{A}_P}{\bar{A}_W}(1-2\,\beta_P)$$

$$\Delta E^{o}_{v\rightarrow P,W} - 3340] \text{ cal/mole} \qquad (77)$$

Equation 77 provides a way to infer $\Delta G^{o}_{v\rightarrow aq,P}$ and therefrom the partition coefficient of a solute between the liquid water phase and the vapor phase from the internal energies involved. The comparison of the calculated values of $\Delta G^{o}_{v\rightarrow aq,P}$ by equation 77 and the experimental values for some of solutes whose data are available in given in Table 7. Differences generally lie within 1 Kcal/mole, which is quite satisfactory,

TABLE 7

DATA FOR CALCULATION OF FREE ENERGY OF SOLUTION FROM THE VAPOR PHASE

AND CALCULATED VALUES OF FREE ENERGY OF SOLUTION AT 25°C.

Solute P	β_P	A_P	$\Delta E^o_{v\to aq,P}$ (cal/mole)	$\Delta E^{o\,vap}_P$ (cal/mole)	$\Delta E^o_{v\to p,W}$ (cal/mole)	$\Delta G^o_{v\to aq,P}$ (calcd.) (cal/mole)	$\Delta G^o_{v\to aq,P}$ (exptl.) (cal/mole)
CCl_4	0.65	102	-5460	7240	-2209	597	123[97]
C_6H_6	0.65	96.3	-6950	7510	-3382	-929	-890[98]
$C_6H_5CH_3$	0.64	109.2	-7710	8490	-3352	-794	-883[98]
$C_6H_5C_2H_5$	0.63	119.6	-9029	9500	-3085	-878	-796[98]
m-$C_6H_4(CH_3)_2$	0.64	120	-9124	9610	-2933	-1055	-842[98]
C_6H_5Cl	0.63	105.8	-5833	9578	-3203	133	-533[99]
o-$C_6H_4Cl_2$	0.62	113.1	-7148	11742	-4765	-942	-1604[100]
CCl_3CH_2Cl	0.63	110.7	-9165	9490	-3862	-1622	-907[101]
CCl_2HCH_2Cl	0.64	99.4	-8349	8800	-4450	-1972	-1951[102]
CCl_3CH_3	0.66	104.3	-7875	7233	-3145	-1120	-255[102]
CH_2ClCH_2Cl	0.66	89.3	-7447	7594	-4595	-2124	-1769[102]
$CHCl_2CH_3$	0.65	93.3	-8131	6692	-4008	-1766	-842[102]
$CHCl_3$	0.66	90.3	-8202	6772	-3991	-824	-1091[103]

considering the inevitable large uncertainty of the measured energies. Improvements could probably be achieved by refining certain assumptions on the method, such as taking both the solute (P) molecules and the water (W) molecules as being spherical. However, the general agreement of experimental results with values predicted from equation 77 argues for the validity of the simple thermodynamic model presented here.

Rearrangement of equation 77 gives

$$\Delta E^{o}_{v\to aq,P} = 2\Delta G^{o}_{v\to aq,P} - (1-2\,\beta_P)\,\Delta E_P^{o\,vap} - 600 + \frac{\bar{A}_P}{\bar{A}_W}\,[(1-2\,\beta_P)\,\Delta E^{o}_{v\to P,W}$$

$$-3340] \quad \text{cal/mole} \tag{78}$$

Again, utilization of relationships

$$\Delta E_P^{o\,vap} = \frac{\Delta G_P^{o\,vap} + 300}{\beta_P} \quad \text{cal/mole} \tag{79}$$

$$\Delta E^{o}_{v\to P,W} = \frac{\Delta G^{o}_{v\to P,W} - 300}{\beta_P} \quad \text{cal/mole} \tag{80}$$

transforms equation 78 to

$$\Delta E^{o}_{v\to aq,P} = 2(\Delta G_P^{o\,vap} + \Delta G^{o}_{v\to aq,P}) - \frac{\Delta G_P^{o\,vap} + 300}{\beta_P} + \frac{\bar{A}_P}{\bar{A}_W}\left(\frac{\Delta G^{o}_{v\to P,W} - 300}{\beta_P}\right.$$

$$\left.-2\Delta G^{o}_{v\to P,W} - 2840\right) \quad \text{cal/mole} \tag{81}$$

Equation 81 enables us to infer the energy of solution of a solute from the vapor phase to the liquid water, $\Delta E^{o}_{v\to aq,P}$, from the measured free energy changes which are related to the solubility of the solute P in the aqueous solution and that of water in P solution.

Thus, $\underset{v\to aq,P}{\Delta E^{o}}$ values can be calculated from equation 81 and information about the orientation energy, $\Delta E^{o}_{orientation}$, can be obtained for an extended number of solutes in aqueous solutions, for which experimental energy data are lacking.

Let us now consider the interesting possibility that the abnormally oriented water molecules surrounding the solute molecule have the ice-I-like structure (this is not, of course, an essential feature of the model and equations developed to this point.). Since the energy of fusion of ice does not change apprecably with temperature, the value 1436 cal/mole at $0^{o}C$ is taken as the molar energy of fusion at $25^{o}C$. Then, the orientation energy is attributed to the transformation of the structure of the liquid water molecules surrounding the solute molecule from the normal structure into the ice-I-like structure. Hence, the number of the "frozen" water molecules surrounding the solute molecule will be inferred from the calculated $\Delta E^{o}_{orientation}$ by the relation.

The number of the water molecules frozen per solute molecule (n)

$$= \frac{\Delta E^{o}_{orientation}\ (cal/mole)}{-1436\quad (cal/mole)} \tag{82}$$

The molar orientation entropy, $\Delta S^{o}_{orientation}$, will be calculated by the relation

$$\Delta G^{o}_{orientation} = \Delta H^{o}_{orientation} - T\Delta S^{o}_{orientation} \tag{83}$$

With the use of equation 73 and the probably good approximation that

$\Delta H^{o}_{orientation} = \Delta E^{o}_{orientation}$, $\Delta S^{o}_{orientation}$ may be expressed as

$$\Delta S^{o}_{orientation} = \frac{1}{2} \frac{\Delta E^{o}_{orientation}}{298.16} \text{ cal/}^{o}\text{K-mole} \qquad (84)$$

The calculated values of $\Delta E^{o}_{orientation}$, $\Delta S^{o}_{orientation}$, the number of the water molecules frozen per molecule of solute (n), and the surface area of the solute molecules divided by the number of the frozen water molecules (which is equal to the interfacial area of the solute facing one molecule of the frozen water)are shown in Table 8.

The fact that the molecular cross section of spherical water is 11.7Å^2 and the surface area of the solute molecule facing one frozen water molecule is approximately constant ($10\pm3\text{Å}^2$ for all the tested solutes and in most cases $10\pm1\text{Å}^2$) is quite remarkable and leads to the following tentative conclusions regarding the nature of dilute aqueous solutions of nonpolar solutes. The solute molecules are surrounded by the ice-I-like structured water molecules, packed tightly, with energies and geometry approximating those of ice. This model requires that only the first layer of the water molecules surrounding the solutes is affected upon introducing a foreign nonpolar or slightly polar solute into pure liquid water. Of course, it would be possible to allow for distribution of the ordered water molecules throughout more than the contact layer, but the simple nature of the conclusions reached here is certainly appealing.

Limited available data and wide discrepancy among existing data make measurements of the reciprocal solubilities of water in organic solvents and organic solvents in water, respectively, desirable for further test of the proposed Interfacial Energy model.

TABLE 8

CALCULATED VALUES OF ORIENTATION ENERGY, ORIENTATION ENTROPY, THE NUMBER OF ORDERED WATER MOLECULES IN CONTACT WITH ONE MOLECULE, AND AVERAGE AREA PER MOLECULE OF WATER AT 25°C

Solutes	$-\Delta E^{o}_{orientation}$ (cal/mole)	$-\Delta S^{o}_{orientation}$ (e.u./mole)	$n=(\frac{-\Delta E^{o}_{orientation}}{1436})$	Surface Area Ap($Å^2$)	Area Per Molecule of Water ($Å^2$)
CCl_4	22858	38.4	15.9	144	9
C_6H_6	17994	30.2	12.5	136	11
$C_6H_5CH_3$	21948	36.8	15.3	153	10
$m\text{-}C_6H_4(CH_3)_2$	24392	40.9	17.0	168	10
C_6H_5Cl	19043	32.0	13.3	148	11
$C_6H_5C_4H_9$	33837	56.8	23.6	197	8
$o\text{-}C_6H_4Cl_2$	21696	36.4	15.0	159	10
C_6H_5I	21563	36.2	15.0	157	10
C_6H_5Br	20862	35.0	14.5	151	10
$n\text{-}C_7H_{16}$	30430	51.1	21.2	190	9
$n\text{-}C_6H_{14}$	28765	48.3	20.0	176	9
$n\text{-}C_8H_{18}$	34671	58.2	24.1	203	8

TABLE 8 Continued

Solutes	$-\Delta E^{o}_{orientation}$ (cal/mole)	$-\Delta S^{o}_{orientation}$ (e.u./mole)	$n=(\frac{-\Delta E^{o}_{orientation}}{1436})$	Surface Area Ap($\AA^2$)	Area Per Molecule of Water ($\AA^2$)
2,2,4-$c_5H_9(CH_3)_3$	33206	55.7	23.1	205	9
c-C_5H_{10}	21896	36.7	15.2	141	9
c-C_6H_{12}	24442	41.0	17.0	155	9
c-$C_5H_9(CH_3)$	24857	41.7	17.3	158	9
c-$C_6H_{11}(CH_3)$	27269	45.8	19.0	172	9
c-C_6H_{10}	20703	34.7	14.4	148	10
$C_6H_5C_2H_5$	23392	39.3	16.3	168	10
CCl_3CH_2Cl	184371	30.9	12.8	155	12
$CHCl_2CH_2Cl$	15838	26.6	11.0	140	13
CCl_3CH_3	20406	32.2	14.2	146	10
CH_2ClCH_2Cl	13458	22.6	9.4	135	13
$CHCl_2CH_3$	16148	27.1	11.2	131	12
$CH_2ClCHClCH_3$	16648	27.9	11.6	144	12
$CHCl_3$	15515	26.0	10.8	126	12

Development of the Interfacial Energy model to a more elaborate degree should enhance our knowledge of aqueous solutions and provide a basis for understanding their abnormal thermodynamic properties. Needless to say, the model should be developed to predict the importance of so-called hydrophobic bonding in biological system.

Brief Summary

The effect of solvents on electron-donor-acceptor complex formation reactions has been studied thermodynamically.

The nonpolar analog model is examined theoretically and methods are developed for using it to predict thermodynamic properties of the transfer of donor, acceptor, complex molecules from the gas phase into dilute solutions in nonpolar solvents. The general problem of inferring free energies of transfer of polar solutes from experimental values of internal energies of transfer is considered. Thermodynamic results calculated by using the NPA model, in conjunction with solubility parameter theory and the Prigogine refined average-potential cell model theory, are compared with experimental results for polar components involved in several molecular complex formation equilibria. For individual solutes, including complexes, calculated and experimental free energies of transfer into hexadecane, diphenylmethane, heptane, cyclohexane, carbontetrachloride, and benzene generally agree to within 0.1 to 0.7 Kcal/mole. Application of the nonpolar analog model has been made for the prediction of solvent effects on molecular complex formation constants. Such effects are not well understood, and the techniques presented here should be quite generally applicable in predicting them.

Energies and free energies of transfer of solutes from the

vapor to the liquid solvent phase to form dilute solutions are calculated in terms of interfacial energies and surface areas. The interfacial energy model has been applied to dilute aqueous solutions to study the orientation effect of abnormally structured water molecules surrounding solute moleclues. The calculated orientation energies which are a direct measure of abnormality of dilute aqueous solutions, lead to tentative conclusions about the picture of solute molecules dissolved in water in dilute aqueous solution: The solute molecules are surrounded by water molecules of the ice-I-like structure, packed tightly; and the abnormal orientation[85] limited primarily to the first layer around the solute molecules.

APPENDIX I

DISTRIBUTION OF SOLUTES BETWEEN THE GAS PHASE AND NONPOLAR SOLVENTS[153]

Frequent use has been made of empirical linear relations among the thermodynamic variables pertaining to the transfer of solutes from one phase to another. For example, Bell[105] and Barclay and Butler[37] showed that the entropy of vaporization of gases from dilute solution in nonpolar and moderately polar solvents varies linearly with the enthalpy of vaporization. More recently, Hildebrand, et al.,[118] have demonstrated the linearity of the entropy of vaporization of gases in nonpolar solvents with the logarithm of their solubilities or their free energies of solution. Research from this laboratory has indicated the utility of linear relations between the free energy and energy of transfer of solutes from one phase to another in predicting the effects of solvents on molecular complex formation equilibria. The following is a description of a convenient method for using linear relations of these types in predicting the solubilities of gases and vapors over a wide range of temperatures.

METHOD OF CALCULATION

Consider the distribution of a solute (i) between the vapor phase (V) and a nonpolar solvent (S). In the dilute solution region,

where i obeys the ideal gas equation in the vapor phase and Henry's law in the condensed phase, the partition coefficient for i is constant (at constant temperature) and defined by

$$K_{D_i} = [i(s)]/[i(v)] \tag{1}$$

where [i(s)] and [i(v)] are the equilibrium molar concentrations of i in $\underline{S}$ and $\underline{V}$, respectively. We assume that the vapor pressure of the solvent is not great enough to cause the fugacity of the gas to differ significantly from its partial pressure, calculated from Dalton's law and the ideal gas equation. Using the unit molarity ideal dilute solution standard states for i (in both phases), expressions may be derived to relate the internal energy and Gibbs free energy of transfer of solutes from $\underline{V}$ to $\underline{S}$. Thus,

$$\Delta G^{o}_{\underline{V}\rightarrow\underline{S},i} = -RT\ell nK_{D,i} \tag{2}$$

and

$$\Delta E^{o}_{\underline{V}\rightarrow\underline{S},i} = RT^2(d\ell nK_{D,i}/dT) + a_s RT^2 \tag{3}$$

where a_s is the coefficient of thermal expansion of the pure solvent. Note that $K_{D,i}$ may be calculated from the partial pressure of the solute (p_i) and its mole fraction in the condensed phase (x_i) by the relation

$$K_{D,i} = x_i RT/p_i \bar{V}_s \tag{4}$$

where $\bar{V}_s$ is the molar volume of the solvent. Equations 1-4 apply also

to the pure solvent itself, where $x_i = 1$, $[S(s)] = 1/\bar{V}_s$ and $[S(v)] = p_s^o/RT$. The vapor pressure of pure solvent (p_s^o) is assumed to be small enough so that the vapors of the solvent may be treated as ideal.

One reason for casting the thermodynamic equations in the somewhat unfamiliar forms given here (equations 1-4) is the simplicity of the linear free energy-internal energy relations which can be derived for solutes if the unit molarity states are used. Figure 4 in Chapter II shows a plot of $\Delta G^o_{v\to s,i}$ vs. $\Delta E^o_{v\to s,i}$ at 25° for a number of solutes in cyclohexane, including the point (x) which pertains to the transfer of the solvent from vapor to condensed phase. The intercept at $\Delta E^o_{v\to s,i} = 0$ is approximately $\Delta G^o_{v\to s,i} = 300$ cal/mole which correspondes to an entrophy of transfer of about -3 entropy units. Thus, the transfer of a solute which dissolves in the solvent with no change in partial molar internal energy occurs with an entropy change of about -3R/2. Although it might be interesting to speculate about the origin of this entropy term, it is more useful in relation to the present discussion to note that very nearly the same intercept value (vis., $\Delta G^o_{v\to s,i} = 300$ cal/more at $\Delta E^o_{v\to s,i} = 0$) obtains for all of the nonpolar solvents for which plots of $\Delta G^o_{v\to s,i}$ vs. $\Delta E^o_{v\to s,i}$ have been constructed. Thus, the simple equation

$$\Delta G^o_{v\to s,i} = \beta_s \Delta E^o_{v\to s,i} + 300 \text{ cal/mole} \qquad (5)$$

where β_s is a constant characteristic of the solvent alone, summarizes a large amount of information about the transfer of solutes into nonpolar media at 25°. Values of β_s are nearly equal to 0.60 for many common organic solvents, excluding flurocarbons. For example, $\beta_s =$ 0.59, 0.63, 0.65, 0.65 and 0.51, respectively, for the solvents heptane,

benzene, cyclohexane, carbon tetrachloride, and perfluoroheptane. It should be emphasized that once the intercept value (300 cal/mole) has been accepted as correct for nonpolar solvents in general, no fitting parameters are required in drawing lines such as that which correlates transfer free energies and energies (displayed as in Figure 5) or in calculating values of β_s to use in equation 5. β_s is calculated by using equation 5 with experimental values of the transfer energy and free energy of the pure solvent at 25°.

Hildebrand, et al.,[118, 119] have observed that the existence of linear correlation of entropy of solution with $-R \log_{10} x_i$ indicates the feasibility of predicting the temperature dependence of the solubility of a gas in a given solvent from the value of its solubility at a single temperature. The simple form of equation 5, and its apparent generality, permit predictions of this type to be made in a straightforward way, using only constants derivable from experimentally known properties of the solvent. We start with the observation that $\log_{10} K_{D,i}$ commonly varies linearly with T^{-1} over a relatively wide range of temperature, where i represents either the solvent or any solute distributed between vapor and condensed phase. Next, we note that if this linear relation holds exactly, equation 3 requires that $\Delta E^{o}_{v \to s,i} - a_s RT^2$ will be strictly constant. Equation 3 may then be written in the integrated form

$$\ell n K_{D,i} = - \frac{[\Delta E^{o}_{v \to s,i} - a_s RT^2]_{T = 298} + \text{constant}}{RT} \qquad (6)$$

where the bracketed terms is to be evaluated at a given temperature, in

this case 25°C.

Whether $K_{D,i}$ increases or decreases with increasing temperature depends, therefore, on whether $\Delta E^{o}_{v\rightarrow s,i} - a_s RT^2$ is negative or positive at 25°C. There will exist a critical value of $K_{D,i}$ (say, K^{*}_{D}) toward which $K_{D,i}$ will trend as T increases. That is, if $K_{D,i}$ at 25°C is less than K^{*}_{D}, $K_{D,i}$ will increase with increasing temperature, whereas if $K_{D,i} > K^{*}_{D}$, $K_{D,i}$ will decrease. Combination of equations 2, 5 and 6 leads to an expression from which K^{*}_{D} may be calculated explicitly. Thus, if $K_{D,i} = K^{*}_{D}$,

$$\Delta E^{o}_{v\rightarrow s,i} = a_s RT^2 \text{ (evaluated at } 298^{o}K) = (\Delta G^{o}_{v\rightarrow s,i} - 300 \text{ cal/mole})/\beta_s,$$

$$-R(298.16^{o}K)\ell n K^{*}_{D} = 300 \text{ cal/mole} + a_s\beta_s R(298.16^{o}K)^2,$$

and

$$K^{*}_{D} = \exp\left[\frac{-300 \text{ cal/mole}}{(298.16^{o}K)R} - a_s\beta_s(298.16^{o}K)\right] \qquad (7)$$

For cyclohexane, the critical value of the partition coefficient is calculated to be $K^{*}_{D} = 0.47$, using values of a_s and β_s for the solvent.

In predicting solubilities or partition coefficients of solutes as a function of T, it is useful to invent a hypothetical temperature T^{*}, characteristic of the solvent, at which the $\log_{10}K_{D,i}$ vs. 1/T curves will all intersect and at which $K_{D,i}$ will equal K^{*}_{D}. That a unique intersection point will exist can be shown by a) combining equation 5, 2 and 7 to obtain

$$\ell n\ K_{D,i}\ (\text{at } 298^{\circ}K) = \frac{-\beta_s\ \Delta E^{\circ}_{v\to s,i}}{R(298.16^{\circ}K)} - \frac{300\ \text{cal/mole}}{R(298.16^{\circ}K)},$$

$$\ell n\ K_D^* = \frac{-300\ \text{cal/mole}}{R(298.16^{\circ}K)} - a_s\beta_s(298.16^{\circ}K),$$

and

$$\ell n\ \frac{K_{D,i}(\text{at } 298^{\circ}K)}{K_D^*} = \frac{-\beta_s}{R(298.16^{\circ}K)}\left[\Delta E^{\circ}_{v\to s,i} - a_s R(298.16^{\circ}K)^2\right] \qquad (8)$$

and b) by comparing equation 8 with the definite form of equation 6 which is obtained by setting $K_{D,i} = K_D^*$ at $T = T^*$:

$$\ell n\ \frac{K_{D,i}(\text{at } 298^{\circ}K)}{K_D^*} = -\left(\frac{1}{298.16^{\circ}K} - \frac{1}{T^*}\right)\left[\frac{\Delta E^{\circ}_{v\to s,i} - a_s R(298.16^{\circ}K)^2}{R}\right] \qquad (9)$$

Equation 8 and 9 can both be valid only if $1/298.16^{\circ}K - 1/T^* = \beta_s/298.16^{\circ}K$ or

$$T^* = 298.16^{\circ}K/(1 - \beta_s). \qquad (10)$$

Thus no matter which solute is chosen, the temperature at which $K_{D,i}$ extrapolates to the value K_D^* will be the same, viz., that given by equation 10. In other words, if a_s and β_s are known for a given solvent, values of K_D^* and T^* may be calculated from equation 7 and 10. Then, on a plot of $\log_{10} K_{D,i}$ vs. $1/T$, the single point $(\log_{10} K_D^*,\ 1/T^*)$ may be located, and a family of straight lines may be drawn radiating from the point. Under the assumptions of the present derivation, these lines represent possible partition coefficient curves for solutes in the given

solvent. K_D data for the pure solvent should also fit on a single straight line drawn from the fixed point $(\log_{10}K_D^*, 1/T^*)$.

RESULTS

Figure 14 displays partition coefficient data for several solutes in cyclohexane. The solid lines are curves which can be used to predict the variation of $K_{D,i}$ or the solubility of solute i with temperature. The calculated curves are seen to provide a reliable prediction of the dependence of $K_{D,i}$ on T for most of these solutes. Data for the solvent itself indicate that only in the vicinity of the critical point does departure from linearity become pronounced. Similar data and predicted curves are given in Figure 15 for solutes in the solvent carbon tetrachloride. Again, the results show that evaluation of the coordinates of the single point, $(\log_{10}K_D^*, 1/T^*)$, permits the accurate prediction of partition coefficient curves for a wide variety of solutes in CCl_4.

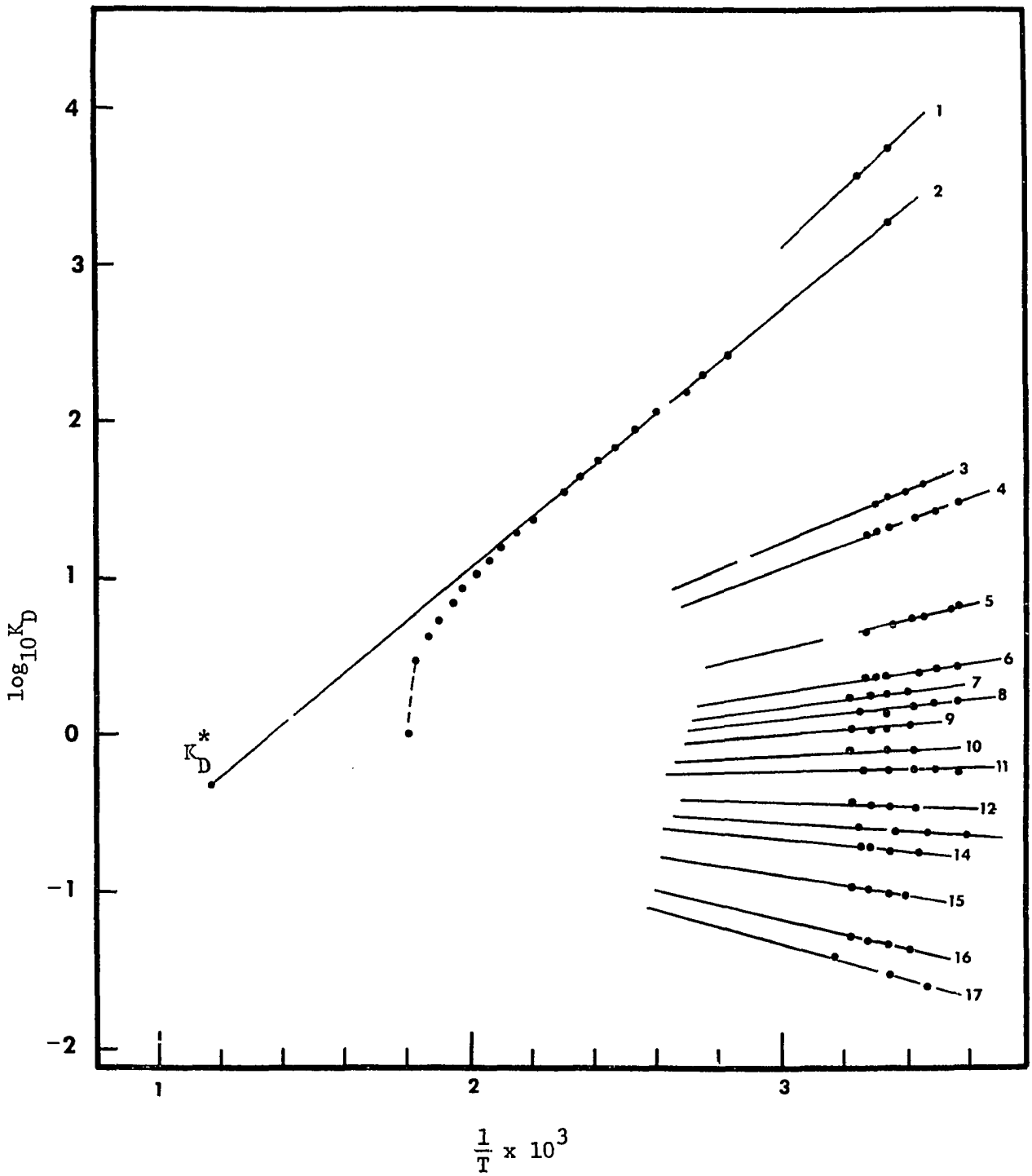


Figure 14: Variation of $K_{D,i}$ with temperature in the cyclohexane solvent.

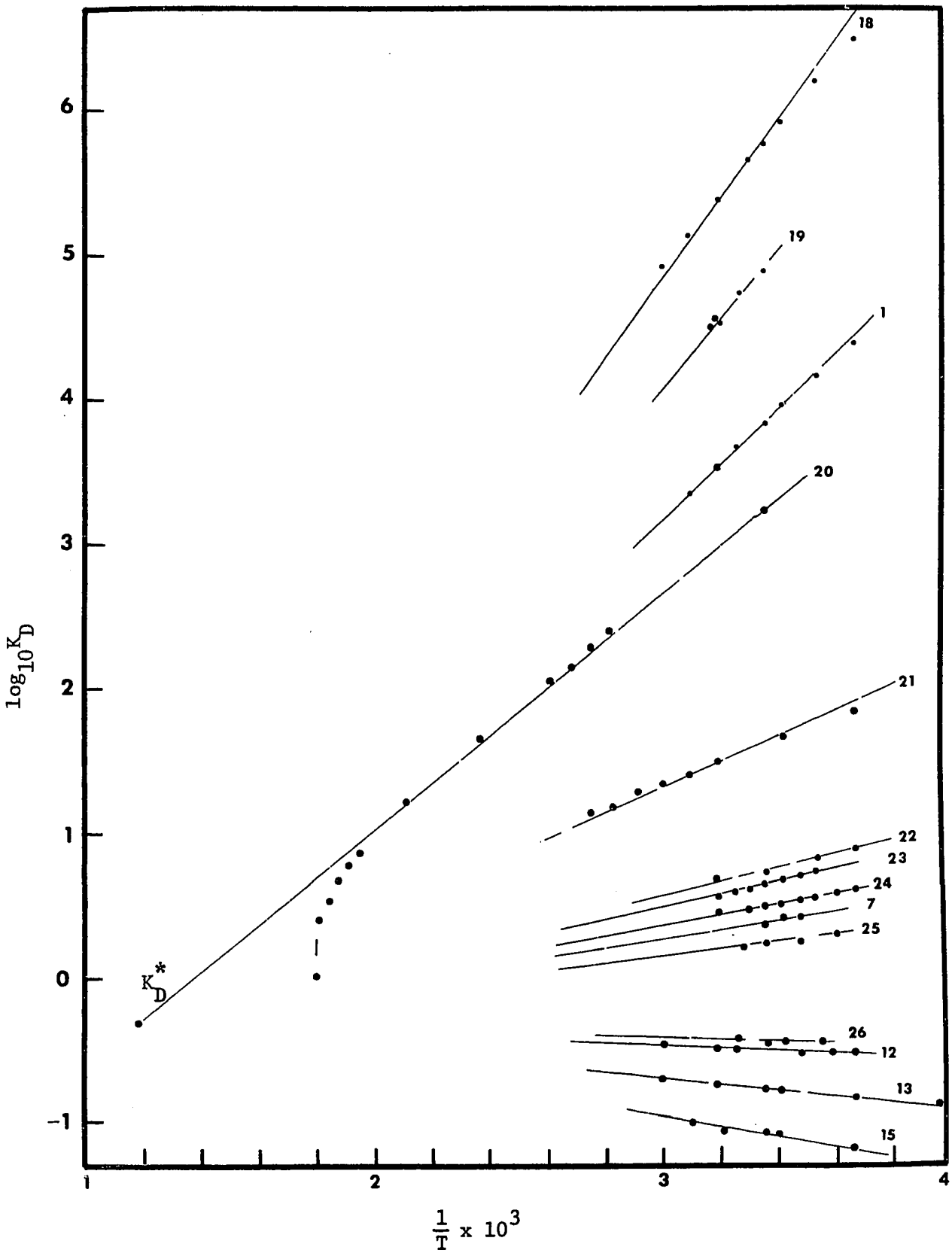


Figure 15: Variation of $K_{D,i}$ with temperature in the carbon tetrachloride solvent.

LEGEND FOR FIGURES 14 and 15

1, I_2[131,140]; 2, c-C_6H_{12}[132]; 3, c-C_3H_6[133]; 4, C_3H_8[134]; 5, c-C_4F_8[134]; 6, $CClF_3$[134]; 7, CO_2[133]; 8, C_3F_8[134]; 9, Kr[133]; 10, CH_4[135]; 11, C_2F_6[134]; 12, Ar[133,147]; 13, CF_4[136]; 14, N_2[133]; 15, H_2[133,148]; 16, Ne[133]; 17, He[137]; 18, C_8H_{10}[138]; 19, P_4[139]; 20, CCl_4[132]; 21, Cl_2[141]; 22, C_2H_6[142]; 23, N_2O[143]; 24, C_2H_2[144]; 25, SF_6[136]; 26, NO[145].

APPENDIX II

A METHOD FOR PREDICTING VAPOR PRESSURES OF NONPOLAR LIQUIDS[154]

It was observed that the vapor pressures at 25°C of numerous nonpolar liquids can be related to their energies of vaporization by the empirical expression

$$\log_{10} P^{o}_{298} = 4.889 - 1.038 \times 10^{-4} \, (\Delta E^{o\,vap}_{298})^{1.15} \qquad (1)$$

where P^{o}_{298} is the equilibrium vapor pressure in Torr and $\Delta E^{o\,vap}_{298}$ is the molar internal energy of vaporization in the liquid in cal/mole at 25°C.[52,53] This relation, used in conjunction with heat of dilution data and various theories of nonpolar liquid mixtures, has been valuable in predicting free energies of transfer of solutes (both polar and nonpolar) from dilute solution in nonpolar solvents to the vapor phase.

Considering the simple form of equation 1, we thought it would be worthwhile to examine its applicability (with modified empirical constants) to liquids at temperatures other than 25°C. The following description outlines the development of an equation which can be used to predict vapor pressures of a nonpolar liquid throughout a range of temperatures from knowledge of the energy of vaporization of the liquid at only one temperature (or, alternatively, from the known vapor

pressure at a single temperature).[64]

DEVELOPMENT OF THE VAPOR PRESSURE EQUATION

Equation 1 may be changed into a form which expresses the molar entropy of vaporization of a nonpolar liquid ΔS^{vap} as a function of the molar volume of the vapor in equilibrium with the liquid ($\overline{V}_{vap}$). Hence, it is related to the familiar Hildebrand Rule,[120] which states that the entropies of vaporization of all normal liquids will be approximately the same if the liquids are compared at equal molar volumes of saturated vapor. Assuming the P^{o}_{298} may be related to $\overline{V}_{vap}$ by the ideal gas equation and neglecting the volume of the liquid in comparison with that of the vapor, we may convert equation 1 into

$$(\Delta S^{vap} - R)^{1.15} = 8.52 + 13.74 \log_{10} \overline{V}_{vap} \qquad (2)$$

where ΔS^{vap} is expressed in entropy units per mole and $\overline{V}_{vap}$ is in liters/mole. In deriving equation 2, the reasonable assumption is made that $\Delta E^{o}{}^{vap} = T\Delta S^{vap} - RT$. An immediate test of equation 2 is provided by substituting into it by the value $\overline{V}_{vap}$ = 49.5 l/mole, from which ΔS^{vap} is calculated to be 22.2 eu/mole; this result agrees well with the observation by Hermsen and Prausnitz[121] that the entropy of vaporization equals 22.4 $\pm$ 0.4 eu/mole for some 20 nonpolar liquids at $\overline{V}_{vap}$ = 49.5 l/mole. However, the significant result here is that to the extent that both equation 1 and the Hildebrand Rules apply, the numerical constants in equation 2 should not depend upon temperature. Therefore, it should be possible to predict $\overline{V}_{vap}$ (and hence the vapor pressure) from ΔS^{vap} alone, or alternatively, from $\Delta E^{o}{}^{vap}$ at the given temperature. In many

cases, of course, the entropy and energy of vaporization will not be known accurately at temperatures of interest; thus, the utility of equation 2 for predicting equilibrium vapor volumes and vapor pressures will be somewhat limited.

Use of Clapeyron equation together with equation 2 leads to a vapor pressure equation which can be applied even when information about the temperature dependence of the energy or entropy of vaporization is lacking. Equation 2 may be written

$$(\Delta E^{o\,vap}/T)^{1.15} = 8.52 + 13.74 \log_{10}\overline{V}_{vap} = 8.52 + 13.74 \log_{10}(RT/P^{o}) \tag{3}$$

and differentiated to give

$$d\,[(\Delta E^{o\,vap}/T)^{1.15}] = 13.74\ d \log_{10}(T/P^{o}) \tag{4}$$

But one form of the Clausius-Clapeyron equation is

$$2.303\ d \log_{10}P^{o}/dT = \Delta E^{o\,vap}/RT^{2} + 1/T$$

or

$$2.303\ d \log_{10}(T/P^{o}) = -(\Delta E^{o\,vap}/RT^{2})\ dT \tag{5}$$

where it is again assumed that the vapor is ideal and that the liquid volume is negligible. Combining equations 4 and 5, we have

$$\frac{d(\Delta E^{o\,vap}/T)^{1.15}}{(\Delta E^{o\,vap}/T)} = -(13.74/2.303RT)\ dT$$

which upon integration, and with substitution of numerical constants, becomes

$$(\Delta E^{o\,vap}/T)^{.15} = -0.902 \log_{10} T + \text{const.}$$

or

$$(\Delta E^{o\,vap}/T)^{.15} = (\Delta E^{o\,vap}/T)^{.15}_{ref} - 0.902 \log_{10}(T/T_{ref}) \qquad (6)$$

Equation 6 permits calculation of $\Delta E^{o\,vap}$ as a function of the absolute temperature, T, given the value of $\Delta E^{o\,vap}$ at a single reference temperature. Using 25°C as the reference temperature, equations 6 and 3 may be combined to give

$$[(\Delta E^{o\,vap}_{298}/298.16)^{.15} - 0.902 \log_{10}(T/298.16)]^{7.67} = 8.52 + 13.74 \log_{10}(RT/P^o) \qquad (7)$$

Equation 7 can be used to predict vapor pressures of a nonpolar liquid at various temperatures , given only $\Delta E^{o\,vap}_{298}$. Moreover, since equation 1 provides a way to calculate $\Delta E^{o\,vap}_{298}$ from P^o_{298}, equation 7 can be used to predict P^o_T from the measured vapor pressure at a single temperature.

APPLICATIONS AND OPTIMIZATION OF EMPIRICAL CONSTANTS

Table 9 includes experimental values of the vapor pressure and temperature for 25 nonpolar liquids, obtained from references 128 and 130. Column 5 lists calculated values of vapor pressure, $P^{o\,calc}$, obtained using equation 7, with values of $\Delta E^{o\,vap}_{298}$ calculated using equation 1 and experimental values of P^o_{298}. Values in parentheses in Column 5 are percent

deviations of calculated from experimental pressures. The root mean square deviation of the logarithm of the calculated pressues is 0.0449, compared to a deviation of 0.0412 in the logarithm of vapor pressures for the same liquids at 25°C, calculated using equation 1.

A slight improvement in fitting the vapor pressure data in Table 9 can be achieved by treating the numerical constants in equation 1 as variable parameters. Thus, if equation 1 is generalized to

$$\log_{10} P^{o}_{298} = a - b(\Delta E^{o\,vap}_{298})^{1.15} \tag{8}$$

equation 2 becomes

$$(\Delta S^{vap} - R)^{1.15} = \frac{a - \log_{10}(298.16\ R)}{298.16^{1.15}\ b} + \frac{\log_{10} \bar{V}_{vap}}{298.16^{1.15}\ b} \tag{9}$$

and 7 becomes

$$[(\Delta E^{o\,vap}_{298}/298.16)^{.15} - \frac{.15 \log_{10} \frac{T}{298.16}}{1.15\ R(298.16)^{1.15}b}]^{(1.15/.15)} =$$

$$\frac{a - \log_{10}(298.16\ R)}{298.16^{1.15}b} + \frac{\log_{10}(RT/P^{o})}{298.16^{1.15}b} \tag{10}$$

Solving equation 8 for $\Delta E^{o\,vap}_{298}$, and substituting into equation 10 gives the result

$$\log_{10} P^{o} = a + \log_{10}(T/298.16) - [(a - \log_{10} P^{o}_{298})^{(.15/1.15)}$$

$$- (.15/1.15) \frac{\log_{10}(T/298.16)}{Rb^{(1/1.15)}298.16}]^{(1.15/.15)} \tag{11}$$

TABLE 9

EXPERIMENTAL AND CALCULATED VALUES OF VAPOR PRESSURE AND TEMPERATURE FOR NONPOLAR LIQUIDS.

Compound	T(°K)	experimental P^o_{298} (torr)	experimental P^o_T (torr)	Method I † calculated P^o_T (torr)	Method II ‡ calculated P^o_T (torr)
benzene	353.26	95.135	760	711.8(-6.3%)	719.8(-5.3%)
	299.24		100	99.9(-.1%)	99.9(-.1%)
toluene	383.78	28.44	760	721.6(-5.1%)	731.2(-3.8%)
	325.10		100	99.1(-.9%)	99.4(-.6%)
ethyl benzene	409.34	9.50	760	715.8(-5.8%)	725.6(-4.5%)
	347.27		100	98.1(-1.9%)	98.5(-1.5%)
o-xylene	417.57	6.60	760	713.8(-6.1%)	723.5(-4.8%)
	354.47		100	97.9(-2.1%)	98.3(-1.7%)
m-xylene	412.26	8.29	760	711.8(-6.4%)	721.5(-5.1%)
	349.98		100	98.0(-2.0%)	98.4(-1.6%)
p-xylene	411.51	8.76	760	721.3(-5.1%)	731.2(-3.8%)
	349.09		100	98.8(-1.2%)	99.2(-.8%)
propyl benzene	432.38	3.37	760	708.8(-6.7%)	718.1(5.5%)
	367.20		100	96.6(-3.4%)	96.9(-3.1%)
mesitylene	437.85	2.683	760	716.6(-5.7%)	726.0(-4.8%)
	372.05		100	98.3(-1.7%)	98.7(-1.3%)
styrene	418.35	5.983	760	688.0(-9.5%)	697.1(-8.3%)
	355.53		100	94.7(-5.3%)	95.1(-4.9%)
pentane	309.23	512.50	760	748.5 (-1.5%)	751.0(-1.2%)
	260.66		100	104.4(+4.4%)	103.2(+3.2%)

Table 9 - continued

Compound	T(°K)	experimental P^{o}_{298} (torr)	experimental P^{o}_{298} (torr)	Method I† calculated P^{o}_{T} (torr)	Method II‡ calculated P^{o}_{T} (torr)
isopentane	301.01	688.0	760	757.6(-.3%)	758.3(-.22%)
	253.00		100	103.0(+3.0%)	101.5(+1.5%)
neopentane	282.66	1286.0	760	774.6(+1.9%)	770.0(+1.3%)
	236.85		100	104.3(+4.3%)	101.7(+1.7%)
hexane	341.90	151.25	760	727.0(-4.3%)	734.1(-3.4%)
	288.97		100	100.7(+.7%)	100.5(+.5%)
heptane	371.58	45.72	760	709.6(-6.6%)	718.6(-5.4%)
	317.93		100	111.9(+11.9%)	112.3(+12.3%)
octane	398.82	14.03	760	688.4(-9.4%)	697.6(-8.2%)
	338.86		100	95.9(-4.1%)	96.3(-3.7%)
isooctane	372.39	49.37	760	765.7(+.75%)	775.8(+2.1%)
	313.82		100	100.9(+.9%)	101.1(+1.1%)
cyclopentane	322.42	317.44	760	740.2(-2.6%)	745.0(-2.0%)
	271.85		100	101.8(+1.8%)	101.1(+1.1%)
cyclohexane	353.89	97.58	760	739.2(-2.7%)	747.7(-1.6%)
	298.70		100	100.0(0%)	100.0(0%)
methylcyclo-hexane	374.09	46.33	760	768.2(+1.1%)	778.3(2.4%)
	315.23		100	101.1(+1.1%)	101.3(+1.3%)
methycyclo-pentane	345.00	137.50	760	740.0(-2.6%)	747.5(-1.6%)
	291.02		100	100.1(+.1%)	100.0(0%)
1-hexene	336.64	186.0	760	732.3(-3.6%)	739.0(-2.8%)
	284.26		100	101.0(+1.0%)	100.6(+.6%)
1-octene	394.44	17.38	760	700.3(-7.9%)	709.8(-6.6%)
	334.78		100	97.0(-3.0%)	97.4(-2.6%)

TABLE 9 - continued

Compound	T(°K)	experimental P^{o}_{298} (torr)	experimental P^{o}_{298} (torr)	Method I† calculated P^{o}_{T} (torr)	Method II‡ calculated P^{o}_{T} (torr)
propane	231.08	7096.0	760	1064.3(+40%)	1017.8(+34%)
	193.52		100	170.1(+70.1%)	157.1(+57.1%)
butane	272.66	1823.0	760	806.6(+6.1%)	797.9(+5.0%)
	228.98		100	114.7(+14.7%)	111.1(+11.1%)
carbontetra-chloride	349.70	115.25	760	741.7(-2.4%)	749.8(-1.3%)
	295.04		100	100.3(+.3%)	100.3(+.3%)
RMSD in $\log_{10} P_T^{calc}$				.04487	.03815

†In Method I the unmodified constants a = 4.889 and b = 1.038×10^{-4} were used to calculate P^{o}_{T}.

‡In Method II the modified values of a = 4.940 and b = 1.051×10^{-4} were employed.

where R equals 1.987 cal $mole^{-1}$ deg^{-1}. Least squares values of the constants a and b were obtained by minimizing the combined sum of squares of deviations of calculated from experimental values of $\log_{10}P^{o}$, including both the points represented in Table 9 and the vapor pressure data at 25°C. The calculated values of P^{o}_{298} were obtained from equation 8, using experimental $\Delta E^{o}_{298}{}^{vap}$ values[128] and chosen values of the parameters a and b; vapor pressures at other temperatures (exhibited in Table 9) were calculated from equation 11. The vapor pressures at 25°C were assigned statistical weights of 2 (relative to values of vapor pressure at other temperatures) in generating the combined sum of squares of residuals. An absolute minimum in the sum of squares of residuals was located by nonlinear least squares analysis; the least squares values of the parameters are a = 4.940 and b = 1.051×10^{-4}. The calculated vapor pressure (and % deviation) values in column 6 in Table 9 were computed using these constants. The root mean square deviation in the logarithm of the $P^{o}{}^{calc.}$ values given in Table 9 (obtained with the refined constants a and b) has been reduced to 0.0382 (or 8.8% in P^{o}) and the corresponding root mean square deviation in the log of the calculated vapor pressures at 25° is 0.0444, only slightly greater than that obtained from the unmodified equation 1. Some of the largest relative errors occur for systems like propane and butane, for which the ideal gas approximation is relatively poor. Omitting these systems from the analysis does not materially change the least squares values of a and b, although it does decrease the root mean square deviations. It may be worthwhile ultimately to extend the present treatment by using fugacity in place of pressure and

correcting for the volume of the liquid in the thermodynamic relations applied to vaporization. However, the equations given here are simple in form and require a minimum of experimental information in their application; it is doubtful that the anticipated improvement in predicted vapor pressures will be sufficient to warrant introducing correction terms to account for vapor phase nonideality and the liquid volume.

It should also be mentioned that the exponent in equations 1, 8 and related expressions may be varied over a considerable range (1.15 ± 0.10) without significantly modifying values of the predicted vapor pressures. The least squares constants a and b are of course changed when a different exponent is used, but the goodness of fit is only slightly worsened.

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